

AD609904

MEMORANDUM
RM-4345-PR
JANUARY 1965

COPY	2	3	R
HARD COPY		3.00	
MICROFICHE		0.75	

88P

THE NUMERICAL SOLUTION OF THE CHEMICAL EQUILIBRIUM PROBLEM

R. J. Clasen

PREPARED FOR:

UNITED STATES AIR FORCE PROJECT RAND

The **RAND** Corporation
SANTA MONICA • CALIFORNIA

ALWAYS COPY

MEMORANDUM

RM-4345-PR

JANUARY 1965

**THE NUMERICAL SOLUTION OF
THE CHEMICAL EQUILIBRIUM PROBLEM**

R. J. Clasen

This research is sponsored by the United States Air Force under Project RAND—Contract No. AF 19(638)-700 monitored by the Directorate of Development Plans, Deputy Chief of Staff, Research and Development, Hq USAF. Views or conclusions contained in this Memorandum should not be interpreted as representing the official opinion or policy of the United States Air Force.

DDC AVAILABILITY NOTICE

Qualified requesters may obtain copies of this report from the Defense Documentation Center (DDC).

Approved for OTS release

The **RAND** *Corporation*

1700 MAIN ST. • SANTA MONICA • CALIFORNIA • 90406

PREFACE

This Memorandum is one in a continuing series of RAND publications dealing with theoretical computational questions arising from the RAND program of research in biology and physiology. The Memorandum contributes to our ability to apply computer technology to the analysis of complex chemical systems by considering the "chemical equilibrium problem," the problem of determining the distribution of chemical species that minimizes the free energy of a system while conserving the mass of each of the chemical elements.

Solutions to the chemical equilibrium problem published up to this time [4,5] apply to those problems for which an estimate of the solution exists. This Memorandum considers a problem for which no estimated solution exists and solves that problem with the maximum precision now available.

The mathematical aspects of this Memorandum should also be of interest in other fields where computational analyses of complex chemical systems are under consideration, e.g., in studies of rocket propulsion systems, planetary atmospheres, re-entry problems, etc.

SUMMARY

In physical chemistry, the "chemical equilibrium problem" is the problem of determining the distribution of chemical species that minimizes the free energy of a system while conserving the mass of each of the chemical elements. The reactions occurring within the chemical system may be quite complex. However, in a great number of cases, the mathematical statement of the problem can be simplified to a particular mathematical form [7,8] involving the minimization of a nonlinear objective function over a set of linear constraints.

This Memorandum presents the numerical solution of the chemical equilibrium problem by describing methods for starting the solution when an initial estimate is not available, and for improving an initial estimate to make it feasible. It presents a first-order method and a second-order method for solving the chemical equilibrium problem in the context of the linear-logarithmic programming problem [4] and provides convergence criteria for the majority of problems of this type that are likely to be attempted.

FOREWORD

In deciding between the languages of mathematics and physical chemistry, we have chosen in this Memorandum to use that of mathematics. The disadvantage of this choice is that the physical chemist may experience some difficulty in immediately identifying certain concepts. The advantage is that mathematical language divorces the methods from the physical assumptions involved in constructing a mathematical model of a physical system.* The mathematical methods are, hence, free to transcend their specific chemical applications.

The methods given here do not solve every problem that is specified in the given mathematical form. The solution of a problem in which some phase vanishes (a degenerate problem) requires further work. Some work has been done on particular degenerate systems [13], but the accurate numerical solution of a large general system of this type has yet to be accomplished. Until recently, a skilled physical chemist could intuitively eliminate the degeneracies of his model and

*The reader is referred to other works for the procedure of constructing the mathematical models of biochemical systems [9-12].

obviate the need for solving a degenerate system. But, as problems grow, eliminating degeneracy becomes increasingly difficult. Frequently, the point at which the problem becomes too large for the physical chemist to decide whether or not to include a phase coincides with the point at which the problem becomes numerically unwieldy. Hopefully, the future will eliminate these difficulties.

Statements about convergence and convergence tests exist, unless otherwise indicated, in the context of finite-accuracy numerics. Statements of this kind do not mean, in the absence of qualification, that no problem exists nor that no machine would serve as a counter example. Rather they are simply descriptions of what was found to occur in actual practice.

No attempt has been made to describe those methods which were tried and found wanting. The methods presented are those which are best for the largest number of cases.

Finally, it should be pointed out that although computing time was a factor, it was considered secondary to accuracy of results.

ACKNOWLEDGMENTS.

The author wishes to thank J. C. DeHaven, E. C. DeLand, F. R. Gilmore, and N. Z. Shapiro for their many constructive comments and suggestions.

CONTENTS

PREFACE	iii
SUMMARY	v
FOREWORD	vii
ACKNOWLEDGMENTS	ix
Section	
1. INTRODUCTION	1
2. THE INITIAL SOLUTION	5
The Projection Method	5
The Linear Programming Method	9
3. THE LINEAR-LOGARITHMIC PROGRAMMING PROBLEM, FIRST-ORDER METHOD	15
4. THE FIRST-ORDER METHOD FOR SOLVING THE CHEMICAL EQUILIBRIUM PROBLEM	21
5. THE LINEAR-LOGARITHMIC PROGRAMMING PROBLEM, SECOND-ORDER METHOD	28
6. THE SECOND-ORDER CHEMICAL EQUILIBRIUM ALGORITHM	33
7. SUMMARY OF THE COMPUTATION PROCEDURE	35
Appendix	
A. A FORTRAN-IV PROGRAM FOR SOLVING THE CHEMICAL EQUILIBRIUM PROBLEM	37
General Description	37
Subroutines	41
Listing	45
Calling Sequence for Simplex Subroutine	56
B. MATRIX NOTATION AND FURTHER PROOFS	67
REFERENCES	79

1. INTRODUCTION

For the purposes of this Memorandum, the chemical equilibrium problem is merely a name we use for a particular mathematical programming problem, i.e., the problem of minimizing a particular nonlinear function $F(x_1, x_2, \dots, x_n)$, defined below, while satisfying the linear restraints or constraints

$$\sum_{j=1}^n a_{ij} x_j = b_i \quad i=1,2,3,\dots,m \quad (1.1)$$

with $x_j \geq 0$ for $j=1,2,\dots,n$ and a_{ij} , b_i given constants. Assuming that the equations of (1.1) are linearly independent, then in order to have a non-trivial problem it can be assumed that $m < n$. The variables x_1, x_2, \dots, x_n can be considered components of a vector (x_1, x_2, \dots, x_n) . Solving the chemical equilibrium problem then is the problem of determining this vector. The variable x_j will be referred to as the " j^{th} component"; also the numerical value of x_j may be referred to as the "component" rather than using the perhaps linguistically correct but cumbersome term "component value."

The components are partitioned into p non-empty subsets called compartments. Let us denote these compartments by $\langle 1 \rangle, \langle 2 \rangle, \dots, \langle p \rangle$. Then if the j^{th} component is in the k^{th} compartment, we will say $j \in \langle k \rangle$, where each component is in exactly one compartment. The number of the compartment that the j^{th} component is in is denoted by $[j]$. Hence $j \in \langle k \rangle$ implies $[j] = k$, and conversely. Each compartment has associated with it a sum defined by

$$S_k = \sum_{j \in \langle k \rangle} x_j . \quad (1.2)$$

The component fraction \hat{x}_j is defined by $\hat{x}_j = \frac{x_j}{S_{[j]}}$ whenever $S_{[j]} > 0$.

The objective function to be minimized over (1.1) is

$$F(x_1, x_2, \dots, x_n) = \sum_{j=1}^n x_j (c_j + \log \hat{x}_j) \quad (1.3)$$

where c_1, c_2, \dots, c_n are given constants, called objective constants.

When an x_j is zero, $\log \hat{x}_j$ is undefined; but we define $0 \log 0$ to equal 0 so that we may evaluate F when

some components are zero. A feasible solution to the chemical equilibrium problem is defined to be any set of non-negative components that satisfies (1.1). The problem is said to be feasible if it has feasible solutions. If no feasible solution is arbitrarily large in any component, the feasible problem is said to be bounded feasible; all practical problems with which one might have occasion to deal are bounded feasible.

A solution or optimal solution to a bounded feasible problem is any feasible solution in which $F(x_1, \dots, x_n)$ attains the minimum value over all feasible solutions. A problem which has optimal solutions in which some component is zero is called degenerate, and a bounded feasible problem in which the components in any optimal solution are all strictly positive is called a non-degenerate problem. It has been shown [1, Theorem 12.1] that a non-degenerate problem has exactly one optimal solution. Hence, we may speak of the solution to the problem. Furthermore, it has also been shown^{*} for the non-degenerate problem that the minimization of F is equivalent to the existence of numbers $\pi_1, \pi_2, \dots, \pi_m$, called Lagrange multipliers, which satisfy:

^{*}Ref. 1, p. 18.

$$\sum_{i=1}^m \pi_i a_{ij} = c_j + \log \hat{x}_j \quad j=1,2,3,\dots,n \quad (1.4)$$

In the following sections we derive conditions, analogous to (1.4), which are useful in solving the problem. In Sec. 2 we are interested in finding a solution to (1.1) with all $x_j > 0$. A set of x_j which satisfies these conditions is called a positive feasible solution. If (1.1) is satisfied with $x_j \geq 0$, we have called such a result a feasible solution. The theory of linear programming gives us methods of finding feasible solutions to problems with linear restraints. In Sec. 2, we use a linear programming technique to find a positive feasible solution. In Sec. 4 we show how to modify the initial positive feasible solution to get the solution to the problem.

2. THE INITIAL SOLUTION

The algorithms presented in the following sections require an initial positive feasible solution in order that the procedure for solving the problem can be initiated. Frequently, an individual with a problem to solve will be able to give a rather accurate estimate of its optimal solution. This estimate may be the exact solution of another problem which differs from the one being considered in relatively minor ways.

THE PROJECTION METHOD

Let us suppose that such is the case, and let us denote the estimate of the components by y_1, y_2, \dots, y_n . These values, substituting y_j for x_j in Eq. (1.1), will not generally satisfy (1.1), being somewhat in error. Let us denote these errors by g_1, g_2, \dots, g_m ; that is, let

$$g_i = b_i - \sum_{j=1}^n a_{ij} y_j \quad i=1, 2, \dots, m \quad (2.1)$$

Then, we wish to find corrections to y_j such that, denoting the corrections by θ_j , we have

$$b_i - \sum_{j=1}^n a_{ij} (y_j + \theta_j) = 0 \quad i=1, 2, \dots, m$$

or

$$g_i = \sum_{j=1}^n a_{ij} \theta_j \quad i=1,2,\dots,m \quad (2.2)$$

The θ_j must also be chosen such that $y_j + \theta_j > 0$, for all j . We cannot guarantee this condition, but we can attempt to choose small values for θ_j . One way to do this is to minimize

$$\sum_{j=1}^n w_j \theta_j^2$$

subject to (2.2), where w_j is the "weight" or relative importance of minimizing θ_j . This reduces to the problem of finding Lagrange multipliers $\pi_1, \pi_2, \dots, \pi_m$, such that with

$$L = \frac{1}{2} \sum_{j=1}^n w_j \theta_j^2 - \sum_{i=1}^m \pi_i \left(\sum_{j=1}^n a_{ij} \theta_j - g_i \right) \quad (2.3)$$

we have

$$\frac{\partial L}{\partial \theta_j} = 0 \quad j=1,2,\dots,n \quad (2.4)$$

Equation (2.4) becomes

$$w_j \theta_j = \sum_{i=1}^m a_{ij} \pi_i \quad j=1,2,\dots,n \quad (2.5)$$

and substituting (2.5) into (2.2) we have

$$g_i = \sum_{\ell=1}^m \left[\pi_{\ell} \left(\sum_{j=1}^n \frac{a_{\ell j} a_{ij}}{w_j} \right) \right], \quad i=1,2,\dots,m \quad (2.6)$$

The terms

$$\sum_{j=1}^n \frac{a_{\ell j} a_{ij}}{w_j}$$

can be immediately evaluated; let us denote these terms

by

$$q_{\ell i} = \sum_{j=1}^n \frac{a_{\ell j} a_{ij}}{w_j} \quad (2.7)$$

Note that $q_{\ell i} = q_{i \ell}$. Then, (2.6) becomes

$$g_i = \sum_{\ell=1}^m q_{\ell i} \pi_{\ell} \quad i=1,2,\dots,m \quad (2.8)$$

Equation (2.8) is a set of m simultaneous equations in the m unknowns, $\pi_1, \pi_2, \dots, \pi_m$. These equations may be solved for $\pi_1, \pi_2, \dots, \pi_m$, and then these values may be substituted in (2.5) to get $\theta_1, \theta_2, \dots, \theta_n$. There remains the question of choosing values for the weighting factors w_j . In tests of this method, it has been found that using

$$w_j = \frac{1}{y_j}$$

yields satisfactory results. The choice of the weighting factors depends, to some extent, on the available computers. Using these weighting factors, we can summarize the computation of θ_j in the following three equations:

$$q_{\ell i} = \sum_{j=1}^n a_{\ell j} a_{ij} y_j \quad \begin{matrix} i=1,2,\dots,m \\ \ell=1,2,\dots,m \end{matrix} \quad (2.9)$$

$$\sum_{\ell=1}^m q_{\ell i} \pi_{\ell} = b_i - \sum_{j=1}^n a_{ij} y_j \quad i=1,2,\dots,m \quad (2.10)$$

$$\theta_j = y_j \sum_{i=1}^m a_{ij} \pi_i \quad j=1,2,\dots,n \quad (2.11)$$

where

$$x_j = y_j + \theta_j \quad j=1,2,\dots,n \quad (2.12)$$

The x_j from (2.12) will satisfy (1.1). However, the x_j need not all be strictly positive. If any x_j is zero or negative, this method of obtaining the initial solution, which we shall call the projection method, has failed. If the projection method fails, or if no initial estimate is provided, then a linear programming method may be used.

THE LINEAR PROGRAMMING METHOD

The terminology used in linear programming is similar to the terminology used above in describing the chemical equilibrium problem. The statement of a linear programming problem includes a set of linear restraints

$$\sum_{j=1}^n a_{ij}x_j = b_i \quad i=1,2,\dots,m \quad (2.13)$$

together with a set of constants $C_1, C_2, C_3, \dots, C_n$, called costs. A feasible solution to a linear programming problem is any set of non-negative x_j such that (2.13) is satisfied. The costs are used to form the following expression, L , which is called the objective function

$$L = \sum_{j=1}^n C_j x_j . \quad (2.14)$$

For every set of feasible x_j , we can evaluate L . The set of feasible x_j for which L has the minimum value that it can have with any set of feasible x_j , is called a solution of the linear programming problem. A problem which has sets of feasible x_j is called a feasible problem, and a problem in which there are no sets of feasible x_j is called an infeasible problem. An infeasible problem has no solutions, while a feasible problem has at least one solution. In this discussion, we will not be concerned as to whether a problem has more than one solution: we will only be concerned with finding a solution to the problem. Since the means of finding a solution to a linear programming problem has been the subject of many papers and books, we will not give an actual method of solving the linear programming problem here. The reader may refer to Dantzig [2] for a complete discussion of the problem.

The problem of finding a feasible solution to a linear programming problem is itself a linear programming problem--that is, it involves finding a solution to the

problem with all C_j equal to zero. With all $C_j = 0$, L in (2.14) is zero for any set of feasible x_j ; hence, L is at its minimum value for any set of feasible x_j . Since L is at its minimum value for any feasible set of x_j , any feasible set of x_j is, by the above definition, a solution to the linear programming problem.

However, we must not only find a feasible solution to the linear programming problem, we must also find a positive feasible solution to the problem. In order to do this, we let

$$x_j = y_j + y_{n+1} \quad j=1,2,\dots,n \quad (2.15)$$

If we can find non-negative values of y_1, y_2, \dots, y_{n+1} which satisfy

$$\sum_{j=1}^n a_{ij}(y_j + y_{n+1}) = b_i \quad i=1,2,\dots,m \quad (2.16)$$

then x_j , as defined by (2.15), will be a feasible solution. If we can somehow assure that y_{n+1} is positive, then all x_j will be positive. Rewriting (2.16), we have

$$\sum_{j=1}^n a_{ij} y_j + \left(\sum_{j=1}^n a_{ij} \right) y_{n+1} = b_i \quad i=1,2,\dots,m \quad (2.17)$$

If we now specify C_1, C_2, \dots, C_{n+1} , we have a linear programming problem in $n+1$ unknowns. In order to guarantee that y_{n+1} is positive, if it is possible for it to be positive, we can maximize y_{n+1} . It is easy to see that we can maximize y_{n+1} by setting

$$L = - y_{n+1} \quad (2.18)$$

which is equivalent to setting $C_1=C_2=C_3=\dots=C_n=0$, $C_{n+1} = -1$. If the solution to the resulting linear programming problem is feasible and $y_{n+1} > 0$, then we have, by (2.15), a positive feasible solution to the analogous chemical equilibrium problem (1.1). If the linear programming problem is feasible but $y_{n+1} = 0$, then the analogous chemical equilibrium problem is degenerate, since there is no strictly positive solution to the problem. However, this is a rather trivial kind of degeneracy, and its occurrence usually indicates that a mistake was made in setting up the problem. Hence, this linear programming method gives us a way of finding a positive feasible solution to the chemical equilibrium problem if the chemical equilibrium problem is non-degenerate.

The positive feasible solution that we obtain by this method will generally not resemble the final solution of the chemical equilibrium problem. The initial positive feasible solution can be improved by the following technique. Define b_{m+1} to be some multiple, between zero and one, of the value of y_{n+1} that was obtained above. Then, adjoin to the linear restraints (2.17) one more restraint of the form $y_{n+1} = b_{m+1}$. Next, solve the linear programming problem with these restraints and with $C_1=c_1$, $C_2=c_2$, ..., $C_n=c_n$, $C_{n+1}=0$ (recall that the lower-case c's here refer to the c's in the chemical equilibrium problem (1.3)). The solution to this linear programming problem will give a set of components more nearly resembling the solution to the chemical equilibrium problem than did the components calculated from Eqs. (2.17) and (2.18). This new solution, in turn, may be improved by solving another linear programming problem (the details of which can be seen in SUBROUTINE LP in Appendix A) and averaging the new solution with the old solution.

In order to solve an elaborate chemical equilibrium problem it is not sufficient to simply use a method which we can prove converges to the correct solution. Proofs of convergence generally assume infinite computational accuracy, but since we are usually limited in practice to

about eight significant digits, the numerical solution will not always converge. However, it has been observed that the closer we can get to the solution by the initial solution methods described above, the greater will be the probability that the numerical procedure will converge. Furthermore, not only will the probability of convergence be greater, but the number of iterations to get to the solution will be fewer, and hence--when an improved initial solution is used--the computation time will be shorter. Unfortunately, the mathematical methods that are available for analyzing convergence of iterative processes do not, in the case of the chemical equilibrium problem, enable us to prove convergence when we are limited to finite mathematical accuracy. Only experience with a particular method will tell us whether it is a useful numerical procedure to use.

In the next section we consider a somewhat more general problem than the chemical equilibrium problem. This problem is considered first because the numerical results take on an especially simple form when the additional generality is admitted.

3. THE LINEAR-LOGARITHMIC PROGRAMMING PROBLEM,
FIRST-ORDER METHOD

In this section we consider the problem of minimizing

$$F(x_1, x_2, \dots, x_N) = \sum_{j=1}^N x_j (c_j + d_j \log x_j) \quad (3.1)$$

while satisfying the linear restraints

$$\sum_{j=1}^N a_{ij} x_j = b_i \quad i=1, 2, 3, \dots, M \quad (3.2)$$

The symbols a_{ij} , b_i , c_j , and d_j denote constants, and x_1, x_2, \dots, x_N are the unknowns that we seek. We restrict the problem to the case that $d_j \neq 0$ for $j = 1, 2, 3, \dots, N$. We note that if $x_j < 0$, the term in (3.1), $x_j(c_j + d_j \log x_j)$, is undefined, whereas if $x_j > 0$ this term is defined. If $x_j = 0$ we define $x_j(c_j + d_j \log x_j) = 0$, since this expression approaches zero as $x_j > 0$ approaches zero. From this discussion, we see that, in order for a solution of Eqs. (3.1) and (3.2) to be defined, we must assume that $x_j \geq 0$ for $j = 1, 2, 3, \dots, N$.

We may attempt to solve this problem using Lagrange multipliers.* In this method we let

$$L = F(x_1, x_2, x_3, \dots, x_N) - \sum_{i=1}^M \left[\pi_i \left(\sum_{j=1}^N a_{ij} x_j - b_i \right) \right]$$

and then set

$$\frac{\partial L}{\partial x_j} = 0$$

for $j = 1, 2, 3, \dots, N$. Performing the partial differentiation, we get

$$c_j + d_j \log x_j + d_j - \sum_{i=1}^M \pi_i a_{ij} = 0, \quad (3.3)$$

$j=1, 2, 3, \dots, N$

or, when rearranged,

$$\log x_j = d_j^{-1} \left[\sum_{i=1}^M \pi_i a_{ij} - c_j - d_j \right]. \quad (3.4)$$

$j=1, 2, 3, \dots, N$

* See Kaplan, Ref. 3, p. 128, or Dantzig, Ref. 2, p. 140.

Exponentiating both sides of (3.4), we get

$$x_j = \exp \left[d_j^{-1} \sum_{i=1}^M \pi_i a_{ij} - d_j^{-1} c_j - 1 \right]. \quad (3.5)$$

$j=1,2,3,\dots,N$

Note that for (3.5) to be a solution to the problem, we must have all $x_j > 0$. We assume, in the remainder of this section, that the solution does have all $x_j > 0$. Then, the problem reduces to the problem of determining the M π_i so that the x_j from (3.5) satisfy (3.2). Equivalently, the $M + N$ equations (3.2) and (3.5) must be satisfied simultaneously by the proper choice of the $M + N$ unknowns, $\pi_1, \pi_2, \dots, \pi_M, x_1, x_2, \dots, x_N$. We now consider two methods of approximating the solution.

In the first method, we suppose that we have an estimate of the x_j which may or may not satisfy (3.2). We denote this estimate by y_j , and, in this method, solve Eqs. (3.2) and (3.4) simultaneously by making a linear approximation to $\log x_j$. Since we have the estimate that x_j is near y_j , we note that the first-order Taylor expansion of $\log x_j$ about y_j is

$$\log x_j = \log y_j + \frac{x_j - y_j}{y_j} + (\text{higher-order terms}) . \quad (3.6)$$

Dropping the higher-order terms, and substituting (3.6) into (3.4) and solving for x_j , we have

$$x_j = y_j \left[d_j^{-1} \sum_{i=1}^M \pi_i a_{ij} - d_j^{-1} c_j - \log y_j \right] . \quad (3.7)$$

$j=1, 2, 3, \dots, N$

Now, if we substitute these x_j into (3.2), we get

$$\sum_{\ell=1}^M \left(\sum_{j=1}^N d_j^{-1} a_{ij} a_{\ell j} y_j \right) \pi_{\ell} = b_i + \sum_{j=1}^N a_{ij} y_j (\log y_j + d_j^{-1} c_j) .$$

$i=1, 2, 3, \dots, M$

Denoting

$$r_{i\ell} = \sum_{j=1}^N d_j^{-1} a_{ij} a_{\ell j} y_j \quad \begin{matrix} \ell=1, 2, 3, \dots, M \\ i=1, 2, 3, \dots, M \end{matrix} \quad (3.8)$$

and

$$s_i = b_i + \sum_{j=1}^N a_{ij} y_j (\log y_j + d_j^{-1} c_j) \quad (3.9)$$

$i=1, 2, 3, \dots, M$

we have

$$\sum_{\ell=1}^M r_{i\ell} \pi_{\ell} = s_i \quad i=1,2,3,\dots,M \quad (3.10)$$

Equation (3.10) is a set of simultaneous equations which can be solved for $\pi_1, \pi_2, \dots, \pi_M$.

With the above results, we can now define the iterative process for the first method. At each iteration we have a set of values for x_1, x_2, \dots, x_N . At the beginning of the iteration these values are called y_1, y_2, \dots, y_N , and at the end of the iteration the values are x_1, x_2, \dots, x_N . If

$$\frac{x_j - y_j}{y_j}$$

is small for each j , then we say we have converged. The magnitude of "small" depends on the nature of the problem. If

$$\frac{x_j - y_j}{y_j}$$

is not small for some j , then we have not converged and the iteration must be repeated. One iteration consists of the following three steps:

- 1) Evaluate terms in Eqs. (3.8) and (3.9), these terms depending on y_1, y_2, \dots, y_N ;
- 2) Solve Eq. (3.10) for $\pi_1, \pi_2, \dots, \pi_M$;
- 3) Substitute $\pi_1, \pi_2, \dots, \pi_M$ into (3.7) to get x_1, x_2, \dots, x_N .

For this problem, in this generality, we can say nothing about whether this iterative process converges. In the next section we will show that the chemical equilibrium problem is a special case of this problem, and one for which, with appropriate modification, this method does converge.

4. THE FIRST-ORDER METHOD FOR SOLVING THE CHEMICAL EQUILIBRIUM PROBLEM

The chemical equilibrium problem is a special case of the linear-logarithmic programming problem. In order to put Eqs. (3.1) and (3.2) into the form of Eqs. (1.1) and (1.3), we first define

$$N = n+p$$

$$M = m+p$$

where, as stated previously, p is the number of compartments in the problem. Then we define a_{ij} , b_i , x_j , and c_j , for $i > m$ and $j > n$, as follows

$$b_i = 0 \qquad i=m+1, m+2, \dots, M \quad (4.1)$$

$$c_j = 0 \qquad j=n+1, n+2, \dots, N \quad (4.2)$$

$$x_{k+n} = S_k \qquad k=1, 2, \dots, p \quad (4.3)$$

$$a_{ij} = \begin{cases} 0 & \text{if } i \leq m, j > n \\ 1 & \text{if } i > m, j \leq n, \text{ and } [j] = i-m \\ 0 & \text{if } i > m, j \leq n, \text{ and } [j] \neq i-m \\ -1 & \text{if } i > m, j > n, \text{ and } i-m = j-n \\ 0 & \text{if } i > m, j > n, \text{ and } i-m \neq j-n . \end{cases} \quad (4.4)$$

For all j , we define

$$d_j = \begin{cases} +1 & \text{if } j \leq n \\ -1 & \text{if } j > n . \end{cases} \quad (4.5)$$

With these definitions, it has been shown [4] that the two problems are identical. Next, we let

$$x_j = y_j + \theta_j \quad (4.6)$$

$$\pi_i = \begin{cases} \pi'_i & i \leq m \\ \pi'_i + \log S_{i-m} + 1 . & i > m \end{cases}$$

Substituting Eqs. (4.1) through (4.6) into (3.7) through (3.10) and simplifying, we have

$$\theta_j = y_j \left[\sum_{i=1}^m a_{ij} \pi'_i - c_j - \log \hat{y}_j + \pi'_{[j]+m} \right] \quad (4.7)$$

$j=1, 2, \dots, n$

$$r_{i\ell} = \begin{cases} \sum_{j=1}^n a_{ij} a_{\ell j} y_j & \ell \leq m, i \leq m \\ \sum_{j \in \langle i-m \rangle} a_{\ell j} y_j & \ell \leq m, i > m \\ \sum_{j \in \langle \ell-m \rangle} a_{ij} y_j & \ell > m, i \leq m \\ 0 & \ell > m, i > m \end{cases} \quad (4.8)$$

$$s'_i = \begin{cases} b_i + \sum_{j=1}^n a_{ij} y_j (c_j + \log \hat{y}_j - 1) & i \leq m \\ \sum_{j \in \langle i-m \rangle} y_j (c_j + \log \hat{y}_j) & i > m \end{cases} \quad (4.9)$$

$$\sum_{\ell=1}^M r_{i\ell} \pi'_\ell = s'_i \quad i=1, 2, \dots, M \quad (4.10)$$

The directional derivative of F in the direction

$(\theta_1, \theta_2, \dots, \theta_n)$ is given by [1, Theorem 8.11] to be

$$\sum_{j=1}^n \theta_j (c_j + \log \hat{y}_j) . \quad (4.11)$$

But, if we compute $\sum_{j=1}^N \frac{\theta_j^2 d_j}{y_j}$ where by (3.7)

$$\theta_{k+n} = S_k \left[\pi_{m+k} - \log S_k - 1 \right] = S_k \pi'_{m+k} \quad (4.12)$$

$k=1, 2, \dots, p$

we show, in Appendix B, that

$$\sum_{j=1}^N \frac{\theta_j^2 d_j}{y_j} = - \sum_{j=1}^n \theta_j (c_j + \log \hat{y}_j) + \sum_{i=1}^m \pi_i \left(b_i - \sum_{j=1}^n a_{ij} y_j \right) . \quad (4.13)$$

Thus, if we assume that (y_1, y_2, \dots, y_n) is feasible, we get the interesting result that the directional derivative of F in the direction $(\theta_1, \theta_2, \dots, \theta_n)$ is

$$\sum_{j=1}^n \theta_j (c_j + \log \hat{y}_j) = - \sum_{j=1}^N \frac{\theta_j^2 d_j}{y_j} \leq 0 . \quad (4.14)$$

However, it is also shown in Appendix B that the equality on the right side of (4.14) holds if and only if the values for y_j are optimal. We further note that if (y_1, y_2, \dots, y_n) is feasible, then

$$\sum_{j=1}^n a_{ij} \theta_j = 0$$

for $i = 1, 2, \dots, m$. Hence, if (y_1, y_2, \dots, y_n) is feasible, then $(y_1 + \lambda \theta_1, y_2 + \lambda \theta_2, \dots, y_n + \lambda \theta_n)$ will be feasible for any λ for which each $y_j + \lambda \theta_j$ is positive.

We now state the first-order chemical equilibrium algorithm:

- 1) Calculate $(\theta_1, \theta_2, \dots, \theta_n)$ using Eqs. (4.7) through (4.10).
- 2) Calculate the directional derivative of F in the direction $(\theta_1, \theta_2, \dots, \theta_n)$ as given by Eq. (4.11); if this quantity is not negative, we are done.
- 3) Calculate

$$\epsilon = \sqrt{\frac{1}{n} \sum_{j=1}^n \left(\frac{\theta_j}{y_j} \right)^2}$$

ϵ is a number that represents the root-mean-square error in (y_1, y_2, \dots, y_n) . If ϵ is less than some given number (say, 0.001), we are done.

4) Calculate the ratio $-y_j/\theta_j$ for every j for which $\theta_j < 0$. Let λ_1 be the minimum of all such ratios and let $\lambda = \min(1, \beta\lambda_1)$, where β is a number less than 1 but close to 1 (say, 0.99). We now perform the following steps until the test at c) below is satisfied:

- a) Let $z_j = y_j + \lambda\theta_j$;
- b) Compute the directional derivative of F at z_j in the direction $(\theta_1, \theta_2, \dots, \theta_n)$: $f(\lambda) = \theta_j(c_j + \log \hat{z}_j)$;
- c) If $f(\lambda) \leq 0$, go directly to step 5);
- d) Replace λ by $\gamma\lambda$, where $0 < \gamma < 1$, e.g., $\gamma = \frac{1}{2} \sqrt{2}$.

5) Finally, replace y_j by $y_j + \lambda\theta_j$ for $j = 1, 2, \dots, n$.

Steps 1-5 are repeated until either the test in step 2 or the test in step 3 is satisfied.

If this process terminates, the solution will be optimal within the specified limits of accuracy. It may happen that the process does not terminate. Since the objective function F is convex^{*} and assuming infinite computational accuracy, non-termination can occur only because the values chosen for λ become smaller on every

^{*}Ref. 1, Theorem 8.13; Ref. 5.

iteration. This will occur only if some y_j is approaching zero, and hence (y_1, y_2, \dots, y_n) is approaching a point at which, if it were the optimal solution, the problem would be degenerate. It is possible for this to happen for a non-degenerate problem for which the initial solution chosen was too far from the optimal solution. Convergence can be guaranteed by imposing the condition that the value of F at the initial solution be less than the value of F at any feasible, degenerate point. However, it is not practical to impose this condition on the initial solution since it may be very difficult to find such a point. In practice, it has been found that round-off errors cause more difficulty than the possible selection of a poor initial solution.

5. THE LINEAR-LOGARITHMIC PROGRAMMING PROBLEM, SECOND-ORDER METHOD

In the first-order method, presented in Sec. 3, the iterative process was initiated with an estimate of the value of x_1, x_2, \dots, x_N . In the second-order method, we assume that the problem is as defined by Eqs. (3.1) and (3.2), but that we have initial estimates for the values of $\pi_1, \pi_2, \dots, \pi_M$. Let us denote these estimates by $\lambda_1, \lambda_2, \dots, \lambda_M$. The x_j can then be evaluated by Eq. (3.5), substituting λ_i for π_i . These x_j , however, probably will not satisfy Eq. (3.2). The problem of the second-order method is to find numbers $\Delta\lambda_1, \Delta\lambda_2, \dots, \Delta\lambda_M$, such that

$$\pi_i = \lambda_i + \Delta\lambda_i \quad i=1,2,\dots,M \quad (5.1)$$

when substituted into (3.5) will give x_j that satisfy (3.2).

In order to accomplish this, we first use the x_j calculated from Eq. (3.5) to get

$$g_i = b_i - \sum_{j=1}^N a_{ij}x_j \quad i=1,2,\dots,M \quad (5.2)$$

where g_i represents the amount that equation i is in error.

Next, we evaluate

$$\frac{\partial g_i}{\partial \lambda_{\ell}}$$

by

$$\begin{aligned} \frac{\partial g_i}{\partial \lambda_{\ell}} &= \frac{\partial}{\partial \lambda_{\ell}} \left[b_i - \sum_{j=1}^N a_{ij} x_j \right] = - \sum_{j=1}^N a_{ij} \frac{\partial x_j}{\partial \lambda_{\ell}} \\ &= - \sum_{j=1}^N a_{ij} \frac{\partial}{\partial \lambda_{\ell}} \left[\exp \left(d_j^{-1} \sum_{h=1}^M \lambda_h a_{hj} - d_j^{-1} c_j - 1 \right) \right] \\ &= - \sum_{j=1}^N a_{ij} d_j^{-1} x_j a_{\ell j} = - r_{\ell i} \end{aligned} \quad (5.3)$$

where $r_{\ell i}$ is given by Eq. (3.8). If we make a very small change, $d\lambda_1, d\lambda_2, \dots$, in $\lambda_1, \lambda_2, \dots$, the change in g_1, g_2, \dots , is given by dg_1, dg_2, \dots , where

$$dg_i = + \sum_{\ell=1}^M \frac{\partial g_i}{\partial \lambda_{\ell}} d\lambda_{\ell} \quad i=1, 2, \dots, M$$

or

$$dg_i = - \sum_{\ell=1}^M r_{\ell i} d\lambda_{\ell} \quad i=1,2,\dots,M \quad (5.4)$$

We would want dg_i to be equal to $-g_i$ as computed by Eq. (5.2). If we make the approximation that

$$\frac{\partial g_i}{\partial \lambda_{\ell}}$$

is constant over the domain considered, we can set

$dg_i = -g_i$, let $d\lambda_{\ell} = \Delta\lambda_{\ell}$, and write

$$g_i = \sum_{\ell=1}^M r_{\ell i} \Delta\lambda_{\ell} \quad i=1,2,\dots,M \quad (5.5)$$

Equation (5.5) consists of M equations in the M unknowns

$\Delta\lambda_1, \Delta\lambda_2, \dots, \Delta\lambda_M$. We may thus solve Eq. (5.5) for

$\Delta\lambda_1, \Delta\lambda_2, \dots, \Delta\lambda_M$ and compute $\pi_1, \pi_2, \dots, \pi_M$ from (5.1). If

the assumption about

$$\frac{\partial g_i}{\partial \lambda_{\ell}}$$

being constant over the domain considered was correct, then

the x_j computed from (3.5) with these values for π_i will satisfy (3.2). However, in general, they will not satisfy (3.2), but, if we were close enough to the solution so that the

$$\frac{\partial g_i}{\partial \lambda_i}$$

did not vary greatly in the domain considered, then the new values for x_j should come closer to satisfying (3.2) than did the first set of x_j .

With this assumption, we may now state the iterative process:

- a) Using the values at hand for $\pi_1, \pi_2, \dots, \pi_M$, evaluate (3.5).
- b) Using the values for x_j obtained in step a, evaluate (5.2). If the $|g_i|$ are sufficiently small, we are done.
- c) Compute $r_{i'}$ using (3.8) and solve (5.5) for $\Delta\lambda_i$.
- d) Denoting the π_i in step a by λ_i , we get new π_i by (5.1).

Steps a-d are repeated until the $|g_i|$, computed in step b, are sufficiently small, or until they show no more improvement.

There is no proof of convergence for this method.

In fact, the method presented here is unlikely to converge unless the starting values of $\pi_1, \pi_2, \dots, \pi_M$ are very good, and even then there may be no convergence. This method may be used on the chemical equilibrium problem after the first-order method has resulted in a reasonably good solution.

If the π_i obtained from (3.10) in the final iteration of the first-order method are used to initiate the second-order method, the accuracy produced by the second-order method will generally be better than that which could be achieved by use of the first-order method only.

6. THE SECOND-ORDER CHEMICAL EQUILIBRIUM ALGORITHM

In order that the second-order linear-logarithmic method be set in the form of a chemical equilibrium problem, the same definitions as given in Sec. 4--i.e., Eqs. (4.1) through (4.5)--are used here. Since the second-order method is best used after the first-order method has been applied, the initial values of π_i for the second-order method must be specified. The first-order method gives a set of π'_i which are related to π_i by Eq. (4.6). The π_i computed by means of (4.6) are appropriate initial values for the second-order method. Using these initial values for π_i , the second-order chemical equilibrium algorithm is an iterative process for which each iteration consists of the following steps:

- 1) Using the current values for $(\pi_1, \pi_2, \dots, \pi_M)$, evaluate x_1, x_2, \dots, x_n by means of (3.5).
- 2) Calculate g_1, g_2, \dots, g_m by means of (5.2) and set $g_{m+1}, g_{m+2}, \dots, g_M$ equal to zero.
- 3) Compute r_{i_i} from (4.8) and solve (5.5) for $\Delta\lambda_1, \Delta\lambda_2, \dots, \Delta\lambda_M$.
- 4) Let

$$P = \max_{i=1}^M |\Delta\lambda_i|.$$

If $P < \delta$, where δ is a small positive number such as 10^{-5} , we are done; otherwise, let $Q = \min\left(\frac{1}{P}, 1\right)$.

5) Replace π_i by $\pi_i + Q \Delta\lambda_i$ for $i = 1, 2, \dots, M$.

Steps 1-5 are repeated until the test at 4) is satisfied.

P should decrease at every iteration; however, when the values for π_i get close to their optimal values, P may not become zero due to round-off error. In order to prevent an endless repetition of steps 1-5 due to the selection of too small a δ , we can test P against the value of P at the previous iteration. If this value has increased over the previous iteration, it can be assumed that this method has obtained as accurate a solution as possible, and we can terminate the iteration process. The reason for inserting the factor Q above is to prevent the π_i from varying too much on one iteration.

7. SUMMARY OF THE COMPUTATION PROCEDURE

The best method for starting the solution of the chemical equilibrium problem depends on whether an estimate for the solution vector is available. The projection method should be used when the problem being solved is a slight variation from a problem previously solved, and in this case, the values used for y_j in (2.9 - 2.12) should be the solution vector to the previous problem. Even when the estimate is no better than an intuitive guess, the projection method may still be used. The linear programming method, then, may be used as a back-up if the projection method produces a non-positive component. Of course, if no estimate is available, the linear programming method would be used immediately to provide an estimate.

The recommended procedure is, then, to use the first-order method until either no further progress can be made with this method or until the amount of change becomes small from iteration to iteration, and then to use the second-order method. It has been found that, for reasonably large problems (say $m = 30$, $n = 100$), the point at which progress ceases in the first-order method usually occurs when the indicated corrections to the components

of the solution vector average about one per cent of the components; that is, when (3.5) is accurate to about two significant digits. A switch to the second-order method at this point usually yields quite accurate results in two iterations of the second-order method. The second-order method usually satisfies (1.1) to an accuracy of about five significant digits on a machine that carries eight significant digits. This accuracy is typically about three orders of magnitude above what is usually obtained in experimental data.

To summarize, the typical procedure for solving a chemical equilibrium problem is the following:

- 1) If an estimate is available, use the projection method to obtain a feasible estimate.
- 2) If step 1 yields a strictly positive estimate, go to step 3, but if the projection method yields non-positive components, or if there was no initial estimate, then use the linear programming method to get an estimate.
- 3) Use the first-order method until one of the tests described in Section 4 is satisfied.
- 4) Use the second-order method as described in Section 6.

Appendix A

A FORTRAN-IV PROGRAM FOR SOLVING THE CHEMICAL EQUILIBRIUM PROBLEM

GENERAL DESCRIPTION

The program described here is a set of FORTRAN-IV subroutines for solving chemical equilibrium problems.

The calling sequence used is merely the statement:

CALL SOLVE

Communication of data into and out of the subroutines is accomplished by a block common statement:

```
COMMON/SLVE/IV(30),TOL(20),NR(55,2),B(55),KN(120),X(121),C(121),  
1  KL(26),NAM(25,2),A(55,121),PIE(65),V1(65),V2(65),V3(65),  
2  V4(65),XMF(120),X1(121),X2(121),X3(121),XBAR(25),R(65,65)
```

The data that must be input before CALL SOLVE is executed consist of the following:

<u>COMMON Location</u>	<u>Quantity</u>
IV(1)	m
IV(2)	M (= m+p)
IV(3)	p
IV(4)	n
IV(6)	Number of the output unit.

<u>COMMON Location</u>	<u>Quantity</u>
IV(7)	Print flag: -1 = minimal amount of messages; 0 = one message per iteration step; +1 = all messages.
IV(9)	Maximum number of iterations to be allowed.
B(i)	b_i , $i = 1, 2, \dots, m$.
X(j)	y_j , $j=1, 2, \dots, m$, where y_j is the initial estimate of the solution. If no estimate is available, set $X(J) = 0$.
C(j)	c_j , $j=1, 2, \dots, n$.
A(i,j)	a_{ij} , $i=1, 2, \dots, m$; $j=1, 2, \dots, n$.

In addition, all components in one compartment must have consecutive subscripts. That is, components $1, 2, 3, \dots, k_1$ must be in compartment 1; components k_1+1, k_1+2, \dots, k_2 must be in compartment 2; ...; and components $k_{p-1}+1, k_{p-1}+2, \dots, k_p$ must be in compartment p. These k's are communicated to the subroutines by setting

$$KL(1) = 1$$

$$KL(2) = k_1+1$$

$$KL(3) = k_2+1$$

$$\vdots$$

$$KL(p) = k_{p-1}+1$$

$$KL(p+1) = k_p+1$$

In other words, $KL(k)$ is the number of the first component in compartment k , and $KL(p+1)$ is equal to $n+1$.

The above are the only numbers that need be set in order that CALL SOLVE will solve the chemical equilibrium problem. However, in order that the program can write messages, in cases of infeasibility, etc., names for the rows, components, and compartments may be input:

<u>COMMON Location</u>	<u>Quantity</u>
NR(I,1), NR(I,2)	Two-word row name for row I.
KN(J)	One-word component name for component J.
NAM (K,1), NAM(K,2)	Two-word compartment name for compartment K.

In addition, TOL(1) through TOL(5) are tolerances used by the program. If they are zero when the program is entered, they are set by the subroutines to nominal values. These values may also be set by the user of the subroutines, in which case the nominal values will not be set in the subroutines. These tolerances are the following:

<u>Tolerance</u>	<u>Nominal Value</u>	<u>Meaning</u>
TOL(1)	0.01	ϵ in step 3 of the first-order method (see Sec. 4).

<u>Tolerance</u>	<u>Nominal Value</u>	<u>Meaning</u>
TOL(2)	10^{-5}	δ in step 4 of the second-order method (see Sec. 6).
TOL(3)	10^{-12}	Minimum value any x_j is allowed to have.
TOL(4)	10^{-6}	Minimum starting value that any component will have is the lesser of TOL(4) and $\frac{1}{2}y_{n+1}$ (see Sec. 2).
TOL(5)	10^{-8}	Problem is assumed to be degenerate if any S_k becomes less than TOL(5).

With the above as input, the statement CALL SOLVE will cause an attempt to solve the chemical equilibrium problem. If, upon completion of this attempt, a solution is obtained, the cell

IV(10)

will contain a 1 and the following data will be in storage:

<u>COMMON Location</u>	<u>Data</u>
X(i)	x_i , $i=1,2,\dots,n$ (the solution).
XBAR(k)	S_k , $k=1,2,\dots,p$.
PIE(i)	π_i , $i=1,2,\dots,m$.
XMF(i)	\hat{x}_i , $i=1,2,\dots,n$.

If IV(10) is not 1, the subroutines have failed to solve the chemical equilibrium problem. The reason for this failure is written on output unit IV(6). In such a case, X(i) will contain the latest value of these quantities.

SUBROUTINES

There are nine subroutines in the set used for the solution of the chemical equilibrium problem. A brief description of these subroutines follows.

1. Subroutine SOLVE

SOLVE is the master subroutine, and is divided into four functional segments. Each segment calls other subroutines which do specific tasks. The four segments are:

- a) The projection and linear programming routines for obtaining the initial solution (lines 18-42).
- b) The first-order method (lines 43-122).
- c) The second-order method (lines 123-163).
- d) Output messages (lines 164-203).

2. Subroutine BAR

BAR calculates the S_k .

3. Subroutine BERROR

BERROR calculates

$$g_i = b_i - \sum_{j=1}^N a_{ij} x_j \quad i=1,2,\dots,M$$

4. Subroutine DEL

DEL sets

$$w_j = \sum_{i=1}^m a_{ij} q_i \quad j=1,2,\dots,n$$

5. Subroutine RCALC

RCALC calculates the r_{ij} array (4.8).

6. Subroutine CLOG

CLOG computes

$$\alpha_j = c_j + \log \hat{x}_j \quad j=1,2,\dots,n$$

7. Subroutine LP

LP sets up the linear programming problems.

8. Subroutine SIMPLE

SIMPLE solves the linear programming problems.

Information is communicated to this routine via a

calling sequence rather than by **COMMON** as in subroutines 1-7. The dimension of A in **SIMPLE** should agree with the dimension of A in the first seven subroutines, but all other dimensions are dummy statements.

9. Subroutine **MATINV**

MATINV solves simultaneous equations. As in **SIMPLE**, no **COMMON** is used. The dimension of A in **MATINV** should agree with that of R (not A) in **SOLVE**. All other dimensions are singly subscripted and are irrelevant as to magnitude.

* * *

Each of the first seven subroutines has a **COMMON** statement which should be the same in all seven. The dimensions of the variables in this **COMMON** statement may be set to the values for the largest problem to be solved. With m, M, p, and n as previously defined, these dimensions must be at least:

<u>Symbol</u>	<u>Minimum Dimension</u>
IV	30
TOL	20
NR	(m,2)
B	m
KN	n
X	n+1
C	n+1
KL	p+1
NAM	(p,2)
A	(m,n+1)
PIE	M
V1,V2,V3,V4	M
XMF	n
X1,X2,X3	n+1
XBAR	p
R	(M,M) .

A listing of these subroutines follows. This listing does not necessarily represent an actual program. The language used was that version of FORTRAN described in [6]. The machine used for the solution of chemical equilibrium problems was the IBM-7044, which uses a floating-point number with eight bits for the exponent and 28 bits for the sign and mantissa.

LISTING

```

SUBROUTINE SOLVE
COMMON/SLVE/IV(30),TOL(20),NR(55,2),B(55),KN(120),X(121),C(121),
1  KL(26),NAM(25,2),A(55,121),PIE(65),V1(65),V2(65),V3(65),
2  V4(65),XMF(120),X1(121),X2(121),X3(121),XBAR(25),R(65,65)
INTEGER PF
EQUIVALENCE (TOL(3),XMIN),(TOL(4),XSTART),(TOL(5),BARMIN)
EQUIVALENCE (IV(1),M),(IV(2),MEND),(IV(3),NCOMP),(IV(4),N,NTOT),
1 (IV(5),NIT),(IV(6),NOT),(IV(7),PF),(IV(8),ITER),(IV(9),ITMAX),
2 (IV(10),IERROR),(IV(11),LASTCP),(IV(12),KE)
DIMENSION DX(1),ALPHA(1),TH(1),G(1)
EQUIVALENCE (G,V1),(DX,X1),(ALPHA,X2),(TH,X3)
IF (TOL(1).LE.0.0) TOL(1) = 0.01
IF (TOL(2).LE.0.0) TOL(2) = 1.E-5
IF (XMIN.LE.0.0) XMIN = 1.E-12
IF (BARMIN.LE.0.0) BARMIN = 1.E-8
IF (ITMAX.LE.0) ITMAX = 40
DO 152 J = 1, NTOT
IF (X(J).LE.0.) GO TO 5
152 CONTINUE
C IF X IS STRICTLY POSITIVE, BEGIN PROJECTION
CALL BAR(X,XBAR)
2 CALL BERROR(ERR)
CALL RCALC
CALL MATINV(R,MEND,G,-1,V2,V3,V4,KE)
IF (KE.NE.0) GO TO 5
CALL DEL(DX,G)
DO 3 K = 1,NCOMP
KTA = KL(K)
KTB = KL(K+1)-1
MK = M + K
DO 4 J = KTA,KTB
X(J) = X(J) * ( 1. + DX(J) + G(MK) )
IF (X(J).LE.0.) GO TO 5
4 CONTINUE
3 CONTINUE
GO TO 7
C LINEAR PROGRAMMING ROUTINE
5 CALL LP(KF)
IF (KF.NE.0) GO TO 10006
7 CALL BAR(X,XBAR)
CALL CLOG(X,XBAR)
FE2 = 1.E+20
C FIRST ORDER METHOD LOOP
DO 899 ITER=1,ITMAX
CALL BERROR(ERR)
DO 7110 I=1,MEND
PIE(I) = 0.
7110 CONTINUE
DO 7111 K = 1, NCOMP
KTA = KL(K)
KTB = KL(K+1) - 1
MK = M + K
DO 7112 J = KTA, KTB
AX = ALPHA(J) * X(J)
PIE(MK) = PIE(MK) + AX
DO 7113 I = 1,M
PIE(I) = PIE(I) + AX * A(I,J)
7113 CONTINUE
7112 CONTINUE
7111 CONTINUE

```

	DO 7114 I = 1,4	S0061
	PIE(I) = G(I) + PIE(I)	S0062
7114	CONTINUE	S0063
	CALL RCALC	S0064
	CALL MATINV(R,MEND,PIE,-1,V2,V3,V4,KE)	S0065
	IF(KE.NE.0) GO TO 10003	S0066
	DMAX = 1.E+20	S0067
	CALL DEL(TH,PIE)	S0068
7105	GNORM=0.	S0069
	TDA = 0.	S0070
	FE = 0.	S0071
	DO 7104 K=1,NCOMP	S0072
	MK = M + K	S0073
	KTA = KL(K)	S0074
	KTB = KL(K+1) -1	S0075
	DO 7103 J = KTA, KTB	S0076
	TH(J) = TH(J) +PIE(MK)- ALPHA(J)	S0077
	GNORM = GNORM + TH(J) **2	S0078
	TH(J) = TH(J) * X(J)	S0079
	TDA = TDA + TH(J) * ALPHA(J)	S0080
	IF (X(J).LT.-DMAX*TH(J)) DMAX = -X(J)/TH(J)	S0081
	FE = FE + X(J) * ALPHA(J)	S0082
7103	CONTINUE	S0083
7104	CONTINUE	S0084
	EPS= SQRT (GNORM/FLOAT (NTOT))	S0085
	DFF = FE - FE2	S0086
	FE2 = FE	S0087
	IF (ITER.EQ.1) GO TO 7120	S0088
	ITER = ITER - 1	S0089
	IF(PF.GE.0) WRITE(NOT,799) ITR, DFF,OPTL,EPS	S0090
7120	OPTL=AMIN1 (1.,.99*DMAX)	S0091
	IF(PF.GT.0)WRITE(NCT,8241) DMAX,OPTL,TDA,ERK	S0092
	IF (EPS.LE.TOL(1)) GO TO 8259	S0093
826	IF (TDA.GE.0.) GO TO 8267	S0094
8267	DO 8265 II=1,54	S0095
	DO 8301 J = 1,N	S0096
	DX(J) = AMAX1(X(J) + OPTL*TH(J) ,XMIN)	S0097
8301	CONTINUE	S0098
	CALL BAR(DX,XBAR)	S0099
	CALL CLOG(DX,XBAR)	S0100
	TDA = 0.	S0101
	DO 8266 J = 1,NTOT	S0102
	TDA = TDA + TH(J)*ALPHA(J)	S0103
8266	CONTINUE	S0104
	IF(PF.GT.0)WRITE(NCT, 8262)II,OPTL, TDA	S0105
	IF (TDA.LT.0.) GO TO 828	S0106
8264	OPTL = OPTL /1.4142	S0107
8265	CONTINUE	S0108
	CALL BAR(X,XBAR)	S0109
	GO TO 8271	S0110
828	DO 8281 J=1,NTOT	S0111
	X(J) = DX(J)	S0112
8281	CONTINUE	S0113
	FE = 0.	S0114
	DO 8231 J=1,N	S0115
	FE = FE + ALPHA(J)*X(J)	S0116
8231	CONTINUE	S0117
8288	CALL SSWCH(5,LABEL)	S0118
	IF (LABEL.NE.2) GO TO 10004	S0119
899	CONTINUE	S0120

C	END OF FIRST ORDER METHOD LOOP	S0121
	GO TO 10002	S0122
6000	ITER1 = ITER + 1	S0123
	PMAX = 1.E+20	S0124
	PMAX1 = 1.E+21	S0125
C	SECOND ORDER METHOD LOOP	S0126
	DO 6002 ITER = ITER1,ITMAX	S0127
	CALL DEL(DX,PIE)	S0128
	DO 6003 K = 1,NCOMP	S0129
	MTA = KL(K)	S0130
	MTB = KL(K+1) - 1	S0131
	DO 6010 J = MTA,MTB	S0132
	XMF(J) = EXP (DX(J) - C(J))	S0133
	X(J) = XMF(J)*XBAR(K)	S0134
6010	CONTINUE	S0135
	IF (XBAR(K).LE.BARMIN) GO TO 10005	S0136
6003	CONTINUE	S0137
	IF (PMAX.LE.TOL(2).OR.(PMAX.GE.PMAX1.AND.PMAX.GE.PMAX2))	S0138
1	GO TO 10001	S0139
	CALL BERROR(ERR)	S0140
6006	CALL RCALC	S0141
	CALL MATINV(R,MEND,G, -1,V2,V3,V4,KE)	S0142
	IF(KE.NE.0) GO TO 10003	S0143
	PMAX2 = PMAX1	S0144
	PMAX1 = PMAX	S0145
	PMAX = 0.	S0146
	DO 6004 I = 1,MEND	S0147
	PMAX =AMAX1 (PMAX, ABS (G(I)))	S0148
6004	CONTINUE	S0149
	IF (PMAX.EQ.0.0) GO TO 10001	S0150
	ZM =AMIN1 (1./PMAX,1.)	S0151
	DO 6005 I = 1,M	S0152
	PIE(I) = PIE(I) + ZM* G(I)	S0153
6005	CONTINUE	S0154
	DO 6011 K = 1,NCOMP	S0155
	MK = M+K	S0156
	XBAR(K) = XBAR(K)* EXP (ZM * G(MK))	S0157
6011	CONTINUE	S0158
	IF (PF.GE.0) WRITE(NOT,6099) ITER,PMAX,ERR	S0159
	CALL SSWTCH(5,LABEL)	S0160
	IF (LABEL.NE.2) GO TO 10004	S0161
6002	CONTINUE	S0162
C	END OF SECOND ORDER METHOD LOOP	S0163
10002	ERROR = 2	S0164
	WRITE(NOT,20002)	S0165
20002	FORMAT(27H ITERATION LIMIT EXCEEDED)	S0166
	ITER = ITMAX	S0167
	GO TO 10000	S0168
10003	ERROR = 3	S0169
	WRITE(NOT,20003) KE	S0170
20003	FORMAT(21H R MATRIX HAS NULLITY,I3)	S0171
	GO TO 10000	S0172
10004	ERROR = 4	S0173
	WRITE(NOT,20004)	S0174
20004	FORMAT(56H SOLVE ROUTINE TERMINATED BECAUSE SENSE SWITCH 5 IS DOWN	S0175
1)		S0176
	GO TO 10000	S0177
10005	ERROR = 5	S0178
	WRITE(NOT,20005) NAM(K,1),NAM(K,2)	S0179
20005	FORMAT(13H COMPARTMENT ,2A6,10H TOO SMALL)	S0180

LASTCP = K	S0181
GO TO 10000	S0182
10006 IERROR = 6	S0183
GO TO 10000	S0184
10001 IERROR = 1	S0185
10000 RETURN	S0186
8241 FORMAT(15H LAMBDA MAX=1PE12.4,13H, OPT LAMBDA=E10.3,6H, TDA=E12	S0187
1.5,16H, MAX ROW ERROR=E12.5)	S0188
8267 IF (PF.GE.0) WRITE (NOT,8268) ITER	S0189
8268 FORMAT(10H ITERATION,14,30H POSITIVE IDA, GO TO METHOD 2)	S0190
GO TO 6000	S0191
8269 IF (PF.GE.0) WRITE (NOT,8270) ITER	S0192
8270 FORMAT(10H ITERATION,14,42H AV THETA LESS THAN TOL(1), GO TO METHO	S0193
1D 2)	S0194
GO TO 6000	S0195
8271 IF (PF.GE.0) WRITE (NOT,8272) ITER	S0196
8272 FORMAT(10H ITERATION,14,36H STEP SIZE TOO SMALL, GO TO METHOD 2)	S0197
GO TO 6000	S0198
8262 FORMAT(10X, 4HSTEP,12, 9H LAMBDA=1PE10.3,6H, TDA=E15.8)	S0199
759 FORMAT(10H ITERATION,14,24H CHANGE IN FREE ENERGY=1PE15.8,12H	S0200
1STEP SIZE=E15.8,10H AV THETA=E12.5)	S0201
6099 FORMAT(10H ITERATION,14,19H MAX CHANGE IN PIE=1PE15.8,15H MAX ROW	S0202
1ERROR=E15.8	S0203
END	S0204

SUBROUTINE BAR(W,WBAR)	W0001
COMMON/SLVE/IV(30),TOL(20),NR(55,2),B(55),KN(120),X(121),C(121),	W0002
1 KL(26),NAM(25,2),A(55,121),PIE(65),V1(65),V2(65),V3(65),	W0003
2 V4(65),XMF(120),X1(121),X2(121),X3(121),XBAR(25),R(65,65)	W0004
EQUIVALENCE (IV(1),M),(IV(2),MEND),(IV(3),NCOMP),(IV(4),N,NIO1),	W0005
1 (IV(5),NIT),(IV(6),NOT),(IV(7),PF),(IV(8),IIER),(IV(9),ITMAX),	W0006
2 (IV(10),IERROR),(IV(11),LASTCP),(IV(12),KE)	W0007
DIMENSION W(1),WBAR(1)	W0008
7 DO 701 K = 1,NCOMP	W0009
KTA = KL(K)	W0010
KTB = KL(K+1) - 1	W0011
WBAR(K) = 0.	W0012
DO 702 J = KTA,KTB	W0013
WBAR(K) = WBAR(K) + W(J)	W0014
702 CONTINUE	W0015
701 CONTINUE	W0016
END	W0017

```
SUBROUTINE BERROR(BMAX)                                B0001
COMMON/SLVE/IV(30),TOL(20),NR(55,2),R(65),KN(120),X(121),C(121), B0002
1  KL(26),NAM(25,2),A(55,121),PIE(65),V1(65),V2(65),V3(65), B0003
2  V4(65),XMF(121),X1(121),X2(121),X3(121),XBAR(25),R(65,65) B0004
EQUIVALENCE (IV(1),M),(IV(2),MEND),(IV(3),NCOMP),(IV(4),N,NTOT), B0005
1 (IV(5),NIT),(IV(6),NCT),(IV(7),PF),(IV(8),ITER),(IV(9),IIMAX), B0006
2 (IV(10),IERROR),(IV(11),LASICP),(IV(12),KE) B0007
DIMENSION G(1) B0008
EQUIVALENCE (G,V1) B0009
DO 101 I = 1,M B0010
  ZT = 0. B0011
  DO 102 J = 1,N B0012
    IF(A(I,J).NL.0.) ZT = ZT + X(J) * A(I,J) B0013
102  CONTINUE B0014
  G(I) = ZT + B(I) B0015
101 CONTINUE B0016
  DO 110 K = 1,NCOMP B0017
    ZT = 0. B0018
    MTA = KL(K) B0019
    MTB = KL(K+1) - 1 B0020
    DO 111 J = MTA,MTB B0021
      ZT = ZT + X(J) B0022
111  CONTINUE B0023
    MK = M + K B0024
    G(MK) = XBAR(K) - ZT B0025
110 CONTINUE B0026
    BMAX = 0. B0027
    DO 120 I = 1,MEND B0028
      IF (ABS(G(I)).GT. ABS(BMAX) ) BMAX = G(I) B0029
120 CONTINUE B0030
  RETURN B0031
END B0032
```

SUBROUTINE DEL(W,Q)	D0001
COMMON/SLVE/IV(30),TOL(20),NR(55,2),B(55),KN(120),X(121),C(121),	D0002
1 KL(26),NAM(25,2),A(55,121),PIL(65),V1(65),V2(65),V3(65),	D0003
2 V4(65),XMF(120),X1(121),X2(121),X3(121),XBAR(25),R(65,65)	D0004
EQUIVALENCE (IV(1),M),(IV(2),MEND),(IV(3),NCOMP),(IV(4),N,N101),	D0005
1 (IV(5),NIT),(IV(6),NOT),(IV(7),PF),(IV(8),ITER),(IV(9),IIMAX),	D0006
2 (IV(10),IERROR),(IV(11),LASTCP),(IV(12),KE)	D0007
DIMENSION W(1),Q(1)	D0008
DO 20 J = 1,N	D0009
WW=0.	D0010
DO 10 I = 1,M	D0011
IF (A(I,J).NE.0.) WW = WW + A(I,J) * Q(I)	D0012
10 CONTINUE	D0013
W(J) = WW	D0014
20 CONTINUE	D0015
RETURN	D0016
END	D0017

SUBROUTINE RCALC	R0001
COMMON/SLVE/IV(30),TOL(20),NR(55,2),B(55),KN(120),X(121),C(121),	R0002
1 KL(26),NAM(25,2),A(55,121),PIE(65),V1(65),V2(65),V3(65),	R0003
2 V4(65),XMF(120),X1(121),X2(121),X3(121),XBAR(25),R(65,65)	R0004
EQUIVALENCE (IV(1),M),(IV(2),MEND),(IV(3),NCOMP),(IV(4),N,NIOI),	R0005
1 (IV(5),NIT),(IV(6),NOT),(IV(7),PF),(IV(8),ITER),(IV(9),ITMAX),	R0006
2 (IV(10),IERROR),(IV(11),LASTCP),(IV(12),KE)	R0007
COMPUTE R	R0008
DO 1 I = 1,MEND	R0009
DO 2 J = 1,I	R0010
R(I,J) = 0.0	R0011
2 CONTINUE	R0012
1 CONTINUE	R0013
DO 10 K = 1,NTOT	R0014
DO 11 I = 1,M	R0015
IF (A(I,K).EQ.0.) GO TO 11	R0016
AIKX = A(I,K) * X(K)	R0017
DO 12 J = 1,I	R0018
IF (A(J,K).NE.0.) R(I,J) = A(J,K) * AIKX + R(I,J)	R0019
12 CONTINUE	R0020
11 CONTINUE	R0021
10 CONTINUE	R0022
DO 20 K = 1,NCOMP	R0023
IH = K + M	R0024
MTA = KL(K)	R0025
MTB = KL(K+1) - 1	R0026
DO 21 L = MTA,MTB	R0027
DO 22 J = 1,M	R0028
IF (A(J,L).NE.0.) R(IH,J) = R(IH,J) + A(J,L) * X(L)	R0029
22 CONTINUE	R0030
21 CONTINUE	R0031
20 CONTINUE	R0032
DO 30 J = 2,MEND	R0033
JL = J-1	R0034
DO 31 I = 1,JL	R0035
R(I,J) = R(J,I)	R0036
31 CONTINUE	R0037
30 CONTINUE	R0038
50 RETURN	R0039
END	R0040

```
SUBROUTINE CLOG(W,WBAR)                                C0001
COMMON/SLVE/IV(30),TCL(20),NR(55,2),B(55),KN(120),X(121),C(121), C0002
1  KL(26),NAM(25,2),A(55,121),PIE(65),V1(65),V2(65),V3(65), C0003
2  V4(65),XMF(120),X1(121),X2(121),X3(121),XBAR(25),R(65,65) C0004
EQUIVALENCE (IV(1),M),(IV(2),MEND),(IV(3),NCOMP),(IV(4),N,NTOT), C0005
1 (IV(5),NIT),(IV(6),NOT),(IV(7),PF),(IV(8),ITER),(IV(9),ITMAX), C0006
2 (IV(10),IEPROR),(IV(11),LASTCP),(IV(12),KE) C0007
DIMENSION W(1),WBAR(1),ALPHA(1) C0008
EQUIVALENCE (X2,ALPHA) C0009
DO 1 K = 1, NCOMP C0010
  KLA = KL(K) C0011
  KLB = KL(K+1)-1 C0012
  DO 2 J = KLA,KLB C0013
    ALPHA(J) = C(J) C0014
    XXX = W(J)/WBAR(K) C0015
    IF(XXX.GT.0.0) ALPHA(J) = C(J)+ALOG(XXX) C0016
2  CONTINUE C0017
1 CONTINUE C0018
RETURN C0019
END C0020
```

```

SUBROUTINE LP (MON)
COMMON/SLVE/IV(30),TOL(20),NR(55,2),B(55),KA(12),X(121),C(121),
1 KL(26),NAM(25,2),A(55,121),PIE(65),V1(65),V2(65),V3(65),
2 V4(65),XMF(120),X1(121),X2(121),X3(121),XBAR(25),R(65,65)
INTEGER PF
EQUIVALENCE (TOL(3),XMIN),(TOL(4),XSTART),(TOL(5),BARMIN)
EQUIVALENCE (IV(1),M),(IV(2),NEND),(IV(3),NCOMP),(IV(4),N+NTOT),
1 (IV(5),NIT),(IV(6),NOT),(IV(7),PF),(IV(8),ITER),(IV(9),ITMAX),
2 (IV(10),IERROR),(IV(11),LASTCP),(IV(12),KE)
DIMENSION XX(1),KOUT(7),CC(1),P(1)
EQUIVALENCE(CC,XMF),(XX,X2),(P,V1)
MON= 0
IF (XSTART.LE.0.0) XSTART = 1.E-6
DO 10 I = 1,M
P(I) = B(I)
A(I,NTOT+1) = 0.0
DO 15 J = 1,NTOT
A(I,NTOT+1) = A(I,NTOT+1) + A(I,J)
15 CONTINUE
10 CONTINUE
DO 1 J = 1,NTOT
CC(J) = 0.0
1 CONTINUE
CC(N+1) = -1.0
C ZERO-TH SIMPLEX IS TO DETERMINE FEASIBILITY
CALL SIMPLE(0,M,N+1,A,P,CC,KOUT,XX,PIE,V2,V3,V4,X3,R)
ZT = XX(N+1)
IF (PF.GE.0)WRITE (NO1,106)KOUT(2),ZT,KOUT(1)
106 FORMAT(12HCSIMPLEX 0,14,29H ITERATIONS, MAX MIN ELEMENT=1PE15.8,
1 12H, CONDITION ,I3)
ZZT =AMIN1(ZT/2.0, XSTART)
DO 104 I = 1,M
P(I) = P(I) - ZZT*A(I,N+1)
104 CONTINUE
200 DO 201 J = 1,NTOT
X(J) = XX(J)
XMF(J) = 1.0
201 CONTINUE
IF (ZT.LE.0..OR.KOUT(1).NE.0) GO TO 40
C SIMPLEX LOOP
FR2=1.E+20
DO 301 NN = 1, NCOMP
DO 302 J = 1, NTOT
CC(J) = C(J) + XMF(J) - 1.0
302 CONTINUE
FN = FLOAT(NN) - 1.0
CALL SIMPLE(1,M,N,A,P,CC,KOUT,XX,PIE,V2,V3,V4,X3,R)
IF (KOUT(1).NE.0) GO TO 50
300 DO 303 J = 1,NTOT
X(J) = XX(J)
X(J) = ( FN*X1(J) + X(J) ) / (FN + 1.0)
X1(J) = X(J)
303 CONTINUE
CALL BAR(X,XBAR)
K = 1
FR = 0.0
DO 310 J = 1,N
IF (J.GE.KL(K+1)) K = K + 1
IF (J.EQ.KL(K).AND.XBAR(K).GT.0.0)FR=FR-XBAR(K)*ALOG(XBAR(K))
IF (X(J).GT.0.0) FR = FR + X(J)*(ALOG(X(J)) + C(J) )

```

	XMF(J) = 0.	L0061
	IF (XBAR(K).NE.0.) XMF(J) = X(J) / XBAR(K)	L0062
310	CONTINUE	L0063
	IF (PF.GE.0) WRITE(NOT,305) NN,KOUT(2),FR	L0064
305	FORMAT(8H SIMPLEX,13,1H,,14,12H ITERATIONS ,8H FR ENG=1PE15.6)	L0066
	IF (FR.GE.FR2) GO TO 399	L0066
	FR2=FR	L0067
301	CONTINUE	L0068
399	DO 400 J = 1,N	L0069
	X(J) = X(J) + ZZT	L0070
400	CONTINUE	L0071
	RETURN	L0072
40	IF (KOUT(1).GT.1) GO TO 50	L0073
	WRITE (NOT,41)	L0074
41	FORMAT(72H THIS PROBLEM IS INFEASIBLE. THE FOLLOWING LINEAR COMBI	L0075
	INATION OF ROWS, /1X)	L0076
	DO 140 I =1,M	L0077
	IF (PIE(I).NE.0.) WRITE(NOT,141) PIE(I),NR(I,1),NR(I,2)	L0078
141	FORMAT(10X,3H+ (,F15.8,5H) * ,2A6)	L0079
140	CONTINUE	L0080
	WRITE (NOT,142)	L0081
142	FORMAT(48H0 LEADS TO THE FOLLOWING INFEASIBLE EQUATION, /1X)	L0082
	DO 150 K =1,NCOMP	L0083
	MTA = KL(K)	L0084
	MTB = KL(K+1) - 1	L0085
	DO 151 J = MTA, MTB	L0086
	D = 0.	L0087
	DO 152 I =1,M	L0088
	D = PIE(I)* A(I,J) + D	L0089
152	CONTINUE	L0090
	IF (D.NE.0.) WRITE (NOT,143) D,KN(J),NAM(K,1),NAM(K,2)	L0091
143	FORMAT(10X,3H+ (,F15.8,5H) * ,A6,4H IN ,2A6)	L0092
151	CONTINUE	L0093
150	CONTINUE	L0094
	D = 0.	L0095
	DO 160 I =1,M	L0096
	D = PIE(I)*B(I) + D	L0097
160	CONTINUE	L0098
	WRITE (NOT,144) D	L0099
144	FORMAT(1H0,15X, 7H+ 0.0 =,F15.8)	L0100
70	MON = 1	L0101
	RETURN	L0102
50	IF (KOUT(1).NE.2) GO TO 60	L0103
	JT = KOUT(7)	L0104
	DO 51 K = 1,NCOMP	L0105
	IF (JT.GE.KL(K)) GO TO 52	L0106
51	CONTINUE	L0107
52	WRITE (NOT,952) KN(JT),NAM(K,1),NAM(K,2)	L0108
952	FORMAT(14H THE VARIABLE ,A6,4H IN ,2A6,33H IS UNBOUNDED AND MUST B	L0109
	IE REMOVED)	L0110
	GO TO 70	L0111
60	WRITE (NOT,960)	L0112
960	FORMAT(60H SIMPLEX ROUTINE HAS FAILED DUE TO EXCESSIVE ROUND-OFF E	L0113
	RROR)	L0114
	GO TO 70	L0115
	END	L0116

Calling Sequence for Simplex Subroutine

The simplex subroutine, SIMPLE, may be used to solve a general linear programming problem of the form: Minimize

$$\sum_{j=1}^n C_j x_j \quad (1)$$

subject to

$$\sum_{j=1}^n a_{ij} x_j = b_i \quad i=1,2,3,\dots,m \quad (2)$$

The a_{ij} is stored in a two-dimensional array, A, with a_{ij} in cell A(i,j); C_j is stored in a one-dimensional array, C, with C_j in cell C(j); and b_i is stored in a one-dimensional array, B, with b_i in cell B(i).

The calling sequence is

CALL SIMPLE(II,M,N,A,B,C,KO,X,P,JH,XX,Y,PE,E)

where

II = 0;

M = No. of rows, m;

N = No. of variables, n;

A, B, C Are as above;

K0 = A subscripted variable of
dimension 7;

X = A subscripted variable of dimension n or more;

P, JH, XX, Y, and PE = Subscripted variables of
dimension m or more; and

E = A subscripted variable of
dimension m^2 or more.

Upon exiting from the subroutine,

X(1),X(2),...,X(n) Contains x_1, x_2, \dots, x_n (the solution);

P(1),P(2),...,P(m) Contains the shadow prices;

K0(1) Contains an 0 if the problem was
feasible, 1 if the problem was
infeasible, 2 if the problem had
an infinite solution, and 3, 4, or
5 if the algorithm did not terminate;

K0(2) The number of iterations taken;

K0(3) The number of pivots performed since
the last inversion;

K0(4) The number of inversions performed;

K0(5) The number of pivot steps performed;

KO(6) A logical variable that is "true"

if and only if the problem was
feasible; and

KO(7) Contains, if the problem had an
infinite solution, the number of
the variable that was infinite.

The dimension of A (line X0009) must agree (at least
in the first subscript) with the dimension of A in the
calling program. The other dimensions need not agree with
those of the calling program.

If an initial basis is available, this basis may be
communicated to the subroutine by letting

$$II = 1 ,$$

$$X(i) = \begin{cases} 0.0 & \text{if variable } i \text{ is not in basis,} \\ (\text{non-zero}) & \text{if variable } i \text{ is in basis,} \end{cases}$$

and the other quantities remain as above.

This subroutine differs from other linear programming
routines in several respects. If the restraints (2) are
linearly dependent, the problem is considered to be in-
feasible. This is the case because the chemical equilibrium
problem cannot be solved if the restraints are dependent.
In addition, this subroutine was written to be as scale-free

as possible; this was accomplished by computing tolerances internally in the subroutine.

C	AUTOMATIC SIMPLEX	REDUNDANT EQUATIONS CAUSE INFEASIBILITY	X0001
	SUBROUTINE SIMPLE(INFLAG,MX,NN,A,B,C,KOUT,KB,P,JH,X,Y,PE,E)		X0002
	DIMENSION	B(1),C(1),KOUT(7),JH(1),X(1),P(1),Y(1),	X0003
	1	KB(1),E(1),PE(1),KO(7)	X0004
		EQUIVALENCE (K,KO(1)),(ITER,KO(2)),(INVC,KO(3)),	X0005
	2	(NUMVR,KO(4)),(NUMPV,KO(5)),(FEAS,KO(6)),(JT,KO(7))	X0006
		EQUIVALENCE (XX,LL)	X0007
C	THE FOLLOWING DIMENSION SHOULD BE THE SAME HERE AS IT IS IN CALLER.		X0008
	DIMENSION A(55,121)		X0009
	LOGICAL FEAS,VER,NEG,TRIG,KL,ABSC		X0010
C			X0011
C		MOVE INPUTS ... ZERO OUTPUTS	X0012
	DO 1341 I = 1,7		X0013
	KO(I) = 0		X0014
1341	CONTINUE		X0015
	M = MX		X0016
	N = NN		X0017
	TEXP = .5**16		X0018
	NCUT = 4*M + 10		X0019
	NVER = M/2 + 5		X0020
	M2 = M**2		X0021
	IF (INFLAG.NE.0) GO TO 1400		X0022
C*	'NEW' START PHASE ONE WITH SINGLETON BASIS		X0023
	DO 1402 J = 1,N		X0024
	KB(J) = 0		X0025
	KQ = .FALSE.		X0026
	DO 1403 I = 1,M		X0027
	IF (A(I,J).EQ.0.0) GO TO 1403		X0028
	IF (KQ.OR.A(I,J).LT.0.0) GO TO 1402		X0029
	KQ = .TRUE.		X0030
1403	CONTINUE		X0031
	KB(J) = 1		X0032
1402	CONTINUE		X0033
1400	IF (INFLAG.GT.1) GO TO 1320		X0034
	DO 1401 I = 1,M		X0035
	JH(I) = -1		X0036
1401	CONTINUE		X0037
C*	'VER' CREATE INVERSE FROM 'KB' AND 'JH'		X0038
1320	VER = .TRUE.		X0039
1121	INVC = 0		X0040
1122	NUMVR = NUMVR + 1		X0041
	DO 1101 I = 1,M2		X0042
	E(I) = 0.0		X0043
1101	CONTINUE		X0044
	MM=1		X0045
	DO 1113 I = 1,M		X0046
	E(MM) = 1.0		X0047
	PE(I) = 0.0		X0048
	X(I) = B(I)		X0049
	IF (JH(I).NE.0) JH(I) = -1		X0050
	MM = MM + M + 1		X0051
1113	CONTINUE		X0052
C		FORM INVERSE	X0053
	DO 1102 JT = 1,N		X0054
	IF (KB(JT).EQ.0) GO TO 1102		X0055
	GO TO 600		X0056
C	600	CALL JMY	X0057
C		CHOOSE PIVOT	X0058
1114	TY = 0.0		X0059
	DO 1104 I = 1,M		X0060

IF (JH(I).NE.-1) GO TO 1104	X0061
IF (ABS(Y(I)).LE.TY) GO TO 1104	X0062
IR = I	X0063
TY = ABS(Y(I))	X0064
1104 CONTINUE	X0065
KB(JT) = 0	X0066
C TEST PIVOT	X0067
IF (TY.LE.TPIV) GO TO 1102	X0068
C PIVOT	X0069
JH(IR) = JT	X0070
KB(JT) = IR	X0071
GO TO 900	X0072
C 900 CALL PIV	X0073
1102 CONTINUE	X0074
C RESET ARTIFICIALS	X0075
DO 1109 I = 1,M	X0076
IF (JH(I).EQ.-1) JH(I) = 0	X0077
1109 CONTINUE	X0078
1200 VER = .FALSE.	X0079
C PERFORM ONE ITERATION	X0080
C* 'XCK' DETERMINE FEASIBILITY	X0081
FEAS = .TRUE.	X0082
NEG = .FALSE.	X0083
DO 1201 I = 1,M	X0084
IF (X(I).LT.C.C) GO TO 1250	X0085
IF (JH(I).EQ.C) FEAS = .FALSE.	X0086
1201 CONTINUE	X0087
C* 'GET' GET APPLICABLE PRICES	X0088
IF (.NOT.FEAS) GO TO 501	X0089
C PRIMAL PRICES	X0090
DO 503 I = 1,M	X0091
P(I) = PE(I)	X0092
503 CONTINUE	X0093
ABSC = .FALSE.	X0094
GO TO 599	X0095
C COMPOSITE PRICES	X0096
1250 FEAS = .FALSE.	X0097
NEG = .TRUE.	X0098
501 DO 504 J = 1, M	X0099
P(J) = 0.	X0100
504 CONTINUE	X0101
ABSC = .TRUE.	X0102
DO 505 I = 1,M	X0103
MM = I	X0104
IF (X(I).GE.C.C) GO TO 507	X0105
ABSC = .FALSE.	X0106
DO 508 J = 1,M	X0107
P(J) = P(J) + E(MM)	X0108
MM = MM + M	X0109
508 CONTINUE	X0110
GO TO 505	X0111
507 IF (JH(I).NE.0) GO TO 505	X0112
IF (X(I).NE.0.) ABSC = .FALSE.	X0113
DO 510 J = 1,M	X0114
P(J) = P(J) - E(MM)	X0115
MM = MM + M	X0116
510 CONTINUE	X0117
505 CONTINUE	X0118
C* 'MIN' FIND MINIMUM REDUCED COST	X0119
599 JT = 0	X0120

BB = 0.0	X0121
DO 701 J = 1,M	X0122
C SKIP COLUMNS IN BASIS	X0123
IF (KB(J).NE.0) GO TO 701	X0124
DT = 0.0	X0125
DO 303 I = 1,M	X0126
IF (A(I,J).NE.0.0) DT = DT + P(I) * A(I,J)	X0127
303 CONTINUE	X0128
IF (FEAS) DT = DT + C(J)	X0129
IF (ABSC) DT = - ABS(DT)	X0130
IF (DT.GE.00) GO TO 701	X0131
BB = DT	X0132
JT = J	X0133
701 CONTINUE	X0134
C TEST FOR NO PIVOT COLUMN	X0135
IF (JT.LE.0) GO TO 203	X0136
C TEST FOR ITERATION LIMIT EXCEEDED	X0137
IF (ITER.GE.NCUT) GO TO 160	X0138
ITER = ITER + 1	X0139
C* 'JMY' MULTIPLY INVERSE TIMES A(.,JT)	X0140
600 DO 610 I = 1,M	X0141
Y(I) = 0.0	X0142
610 CONTINUE	X0143
LL = 0	X0144
COST = C(JT)	X0145
DO 605 I = 1,M	X0146
AIJT = A(I,JT)	X0147
IF (AIJT.EQ.0.) GO TO 602	X0148
COST = COST + AIJT * PE(I)	X0149
DO 606 J = 1,M	X0150
LL = LL + 1	X0151
Y(J) = Y(J) + AIJT * E(LL)	X0152
606 CONTINUE	X0153
GO TO 605	X0154
602 LL = LL + M	X0155
605 CONTINUE	X0156
C COMPUTE PIVOT TOLERANCE	X0157
YMAX = 0.0	X0158
DO 620 I = 1,M	X0159
YMAX = AMAX1(ABS(Y(I)),YMAX)	X0160
620 CONTINUE	X0161
TPIV = YMAX * TEXP	X0162
C RETURN TO INVERSION ROUTINE, IF INVERTING	X0163
IF (VER) GO TO 1114	X0164
C COST TOLERANCE CONTROL	X0165
IF (TRIG.AND.00.GE.-TPIV) GO TO 203	X0166
TRIG = .FALSE.	X0167
IF (BB.GE.-TPIV) TRIG = .TRUE.	X0168
C* 'ROW' SELECT PIVOT ROW	X0169
C AMONG EQS. WITH X=0, FIND MAXIMUM Y AMONG ARTIFICIALS, OR, IF NONE,	X0170
C GET MAX POSITIVE Y(I) AMONG REALS.	X0171
1000 IR = 0	X0172
AA = 0.0	X0173
KQ = .FALSE.	X0174
DO 1050 I = 1,M	X0175
IF (X(I).NE.0.0.OR.Y(I).LE.TPIV) GO TO 1050	X0176
IF (JH(I).EQ.0) GO TO 1044	X0177
IF (KQ) GO TO 1050	X0178
1045 IF (Y(I).LE.AA) GO TO 1050	X0179
GO TO 1047	X0180

1044	IF (KQ) GO TO 1045	X0181
	KQ = .TRUE.	X0182
1047	AA = Y(I)	X0183
	IR = I	X0184
1050	CONTINUE	X0185
	IF (IR.NE.0) GO TO 1099	X0186
1001	AA = 1.0E+20	X0187
C	FIND MIN. PIVOT AMONG POSITIVE EQUATIONS	X0188
	DO 1010 I = 1,M	X0189
	IF (Y(I).LE.TPIV.OR.X(I).LE.0.0.OR.Y(I)*AA.LE.X(I)) GO TO 1010	X0190
	AA = X(I)/Y(I)	X0191
	IR = I	X0192
1010	CONTINUE	X0193
	IF (.NOT.NEG) GO TO 1099	X0194
C	FIND PIVOT AMONG NEGATIVE EQUATIONS, IN WHICH X/Y IS LESS THAN THE	X0195
C	MINIMUM X/Y IN THE POSITIVE EQUATIONS, THAT HAS THE LARGEST ABSF(Y)	X0196
1016	BB = - TPIV	X0197
	DO 1030 I = 1,M	X0198
	IF (X(I).GE.0..OR.Y(I).GE.BB.OR.Y(I)*AA.GT.X(I)) GO TO 1030	X0199
	BB = Y(I)	X0200
	IR = I	X0201
1030	CONTINUE	X0202
C	TEST FOR NO PIVOT ROW	X0203
1099	IF (IR.LE.0) GO TO 207	X0204
C*	'PIV' PIVOT ON (IR,JT)	X0205
C	LEAVE TRANSFORMED COLUMN IN Y(I)	X0206
900	NUMPV = NUMPV + 1	X0207
	YI = -Y(IR)	X0208
	Y(IR) = -1.0	X0209
	LL = 0	X0210
C	TRANSFORM INVERSE	X0211
	DO 904 J = 1,M	X0212
	L = LL + IR	X0213
	IF (E(L).NE.0.0) GO TO 905	X0214
	LL = LL + M	X0215
	GO TO 904	X0216
905	XY = E(L) / YI	X0217
	PE(J) = PE(J) + COST * XY	X0218
	E(L) = 0.0	X0219
	DO 906 I = 1,M	X0220
	LL = LL + 1	X0221
	E(LL) = E(LL) + XY * Y(I)	X0222
906	CONTINUE	X0223
904	CONTINUE	X0224
C	TRANSFORM X	X0225
	XY = X(IR) / YI	X0226
	DO 908 I = 1, M	X0227
	XNEW = X(I) + XY * Y(I)	X0228
	IF (VER.OR.XNEW.GE.0..OR.Y(I).GT.TPIV.OR.X(I).LT.0.) GO TO 907	X0229
	X(I) = 0.0	X0230
	GO TO 908	X0231
907	X(I) = XNEW	X0232
908	CONTINUE	X0233
C	RESTORE Y(IR)	X0234
	Y(IR) = -YI	X0235
	X(IR) = -XY	X0236
	IF (VER) GO TO 1102	X0237
221	IA = JH(IR)	X0238
	IF (IA.GT.0) KB(IA) = 0	X0239
213	KB(JT) = IR	X0240

JH(IR) = JT	X0241
IF (NUMPV.LE.M) GO TO 1200	X0242
C TEST FOR INVERSION ON THIS ITERATION	X0243
INVC = INVC +1	X0244
IF (INVC.EQ.NVER) GO TO 1320	X0245
GO TO 1200	X0246
C* END OF ALGORITHM, SET EXIT VALUES	X0247
C INFINITE SOLUTION	X0248
207 K = 2	X0249
GO TO 250	X0250
C PROBLEM IS CYCLING	X0251
160 K = 4	X0252
GO TO 250	X0253
C FEASIBLE OR INFEASIBLE SOLUTION	X0254
203 K = 0	X0255
250 IF (.NOT.FEAS) K = K + 1	X0256
DO 1399 J = 1,N	X0257
XX = 0.0	X0258
KBJ = KB(J)	X0259
IF (KBJ.NE.0) XX = X(KBJ)	X0260
KB(J) = LL	X0261
1399 CONTINUE	X0262
C SET 'KOUT'	X0263
1392 DO 1393 I = 1,7	X0264
KOUT(I) = K(I)	X0265
1393 CONTINUE	X0266
RETURN	X0267
END	X0268

C	MATRIX INVERSION WITH ACCOMPANYING SOLUTION OF LINEAR EQUATIONS	M0001
	SUBROUTINE MATINV(A,N,B,M,INA,INB,IP,ISING)	M0002
C		M0003
	DIMENSION B(1),INA(1),INB(1),IP(1)	M0004
	LOGICAL IP	M0005
	DIMENSION A(65,65)	M0006
C		M0007
C	INITIALIZATION	M0008
	DO 20 J = 1,N	M0009
	IP(J) = .FALSE.	M0010
20	CONTINUE	M0011
C	BIG LOOP ON I	M0012
	DO 575 I = 1,N	M0013
	AMAX = 0.0	M0014
C	SEARCH FOR PIVOT ELEMENT	M0015
	DO 105 J = 1,N	M0016
	IF (IP(J)) GO TO 105	M0017
	DO 100 K = 1,N	M0018
	IF (IP(K) .OR. ABS(AMAX).GE.ABS(A(J,K))) GO TO 100	M0019
	IROW = J	M0020
	ICOL = K	M0021
	AMAX = A(J,K)	M0022
100	CONTINUE	M0023
105	CONTINUE	M0024
	IF (AMAX.EQ.0.0) GO TO 750	M0025
	IP(ICOL) = .TRUE.	M0026
C	INTERCHANGE ROWS TO PUT PIVOT ELEMENT ON DIAGONAL	M0027
	IF (IROW.EQ.ICOL) GO TO 260	M0028
	DO 200 L = 1,N	M0029
	SWAP = A(IROW,L)	M0030
	A(IROW,L) = A(ICOL,L)	M0031
	A(ICOL,L) = SWAP	M0032
200	CONTINUE	M0033
	IF (M.EQ.0) GO TO 260	M0034
	SWAP = B(IROW)	M0035
	B(IROW) = B(ICOL)	M0036
	B(ICOL) = SWAP	M0037
260	INA(I) = IROW	M0038
	INB(I) = ICOL	M0039
C	DIVIDE PIVOT ROW BY PIVOT ELEMENT	M0040
	A(ICOL,ICOL) = 1.0	M0041
	DO 350 L = 1,N	M0042
	A(ICOL,L) = A(ICOL,L) / AMAX	M0043
350	CONTINUE	M0044
	IF (M.NE.0) B(ICOL) = B(ICOL) / AMAX	M0045
C	COMPLETE THE PIVOT	M0046
380	DO 550 LL = 1,N	M0047
	IF (LL.EQ.ICOL) GO TO 550	M0048
	SWAP = A(LL,ICOL)	M0049
	A(LL,ICOL) = 0.0	M0050
	DO 450 L = 1,N	M0051
	A(LL,L) = A(LL,L) - A(ICOL,L) * SWAP	M0052
450	CONTINUE	M0053
	IF (M.NE.0) B(LL) = B(LL) - B(ICOL) * SWAP	M0054
550	CONTINUE	M0055
575	CONTINUE	M0056
600	IF (M.LT.0) RETURN	M0057
C	INTERCHANGE COLUMNS	M0058
	DO 710 I = 1,N	M0059

```
      L = N + 1 - I
      IF (INA(L).EQ.INB(L)) GO TO 710
      IROW = INA(L)
      ICOL = INB(L)
      DO 705 K = 1,N
        SWAP = A(K,IROW)
        A(K,IROW) = A(K,ICOL)
        A(K,ICOL) = SWAP
705    CONTINUE
710  CONTINUE
740  RETURN
C SINGULARITY FLAG
750  ISING = 1 + N - I
      GO TO 600
      END
```

```
M0060
M0061
M0062
M0063
M0064
M0065
M0066
M0067
M0068
M0069
M0070
M0071
M0072
M0073
M0074
```

Appendix B

MATRIX NOTATION AND FURTHER PROOFS

The derivations in the preceding sections would be facilitated by the use of matrix notation rather than subscripted variables. We introduce the following symbols to correspond to the subscripted variables used in Sec. 3.

<u>Subscripted Variable</u>	<u>Matrix</u>	<u>Size of Matrix</u>
a_{ij}	A	MxN
b_i	B	Mx1
y_j	Y	Nx1
d_j	D	Nx1
c_j	C	Nx1
π_i	π	Mx1
r_{il}	R	MxM
x_j	X	Nx1

The single-column matrices may also be thought of as vectors. We use here the convention that an operator applied to a matrix means that the operator operates on each element of the matrix. For example, $\log Y$ is the Nx1 matrix consisting of

$$\begin{pmatrix} \log y_1 \\ \log y_2 \\ \vdots \\ \log y_N \end{pmatrix}$$

The superscript T indicates the transposition of a matrix. We assume that the elementary results of matrix theory are known. For example, it is known that the inverse of an invertible symmetric matrix is symmetric. The square diagonal matrix whose diagonal is one of the vectors previously defined will be denoted by the previously defined vector in elongated type; that is,

$$\mathbb{D} = \text{diag } (D)$$

and

$$\mathbb{Y} = \text{diag } (Y)$$

Equations (3.2) and (3.7) in matrix notation are

$$AX = B \tag{B.1}$$

$$X = \mathbb{Y} (\mathbb{D}^{-1} A^T \pi - \mathbb{D}^{-1} C - \log Y) . \tag{B.2}$$

To see the ease of matrix notation, we may substitute (B.2) into (B.1) to get

$$AYD^{-1}A^T\pi = B + AY(D^{-1}C + \log Y) . \quad (B.3)$$

By letting

$$R = AYD^{-1}A^T \quad (B.4)$$

and

$$S = B + AY(D^{-1}C + \log Y) , \quad (B.5)$$

we see that

$$R\pi = S \quad (B.6)$$

corresponds to (3.10).

In Sec. 4, we evaluated

$$\sum_{j=1}^N \frac{\theta_{ji}^2}{y_j} \quad (B.7)$$

but we did not give the details of the computation. The algebra of this evaluation is very difficult unless matrix algebra is used. In matrix notation, (B.7) is $\theta^T D Y^{-1} \theta$, where $\theta = X - Y$. From (B.2) we have

$$\theta = Y (D^{-1} A^T \pi - D^{-1} C - \log Y) - Y. \quad (B.8)$$

Hence,

$$\begin{aligned} \theta^T D Y^{-1} \theta &= (\pi^T A D^{-1} - C^T D^{-1} - \log Y^T) Y D Y^{-1} \theta - Y^T D Y^{-1} \theta \\ &= \pi^T A (D^{-1} Y D Y^{-1}) \theta - (C^T D^{-1} + \log Y^T) D Y Y^{-1} \theta - Y^T Y^{-1} D \theta \\ &= \pi^T A \theta - (C^T D^{-1} + \log Y^T) D \theta - D^T \theta. \end{aligned} \quad (B.9)$$

Since $AX = B$, $A\theta = AX - AY = B - AY$. Also, in the chemical equilibrium formulation,

$$D^T \theta = \sum_{j=1}^n \theta_j - \sum_{j=n+1}^N \theta_j = \sum_{k=1}^p \left(\sum_{j \in \langle k \rangle} \theta_j - \theta_{k+m} \right) = 0$$

and

$$\begin{aligned}
 & (C^T \mathbb{I}^{-1} + \log Y^T) \mathbb{I} \theta \\
 &= \sum_{j=1}^n (c_j + \log y_j) \theta_j + \sum_{j=n+1}^N \log y_j (-\theta_j) \\
 &= \sum_{k=1}^p \left(\sum_{j \in \langle k \rangle} \theta_j (c_j + \log y_j) - \theta_k \log S_k \right) \\
 &= \sum_{k=1}^p \left(\sum_{j \in \langle k \rangle} \theta_j (c_j + \log y_j - \log S_k) \right) \\
 &= \sum_{j=1}^n \theta_j (c_j + \log \hat{y}_j) .
 \end{aligned}$$

Hence,

$$\sum_{j=1}^N \frac{\theta_j^2 d_j}{y_j} = \sum_{i=1}^m \pi_i \left(b_i - \sum_{j=1}^n a_{ij} y_j \right) - \sum_{j=1}^n \theta_j (c_j + \log \hat{y}_j) \quad (\text{B.10})$$

in the context of the chemical equilibrium problem used in Sec. 4.

Next we wish to show that

$$\sum_{j=1}^N \frac{\theta_j^2}{y_j} \geq 0$$

as stated in (4.14). First, we prove

Lemma 1: Let y_1, y_2, \dots, y_r be positive numbers and let $\theta_1, \theta_2, \dots, \theta_r$ be any real numbers. Let

$$G = \sum_{j=1}^r \frac{\theta_j^2}{y_j} - \frac{\left(\sum_{j=1}^r \theta_j \right)^2}{\sum_{j=1}^r y_j}.$$

Then,

- i) $G \geq 0$
- ii) $G = 0$ if and only if

$$\frac{\theta_1}{y_1} = \frac{\theta_2}{y_2} = \dots = \frac{\theta_r}{y_r}.$$

Proof: Let $\alpha_j = \theta_j / y_j$, $j=1, 2, \dots, r$. Then,

$$G = \sum_{j=1}^r \alpha_j^2 y_j - \frac{\left(\sum_{j=1}^r \alpha_j y_j \right)^2}{\sum_{j=1}^r y_j}$$

$$\begin{aligned}
 &= \left(\sum_{j=1}^r y_j \right)^{-1} \left[\left(\sum_{j=1}^r y_j \right) \left(\sum_{j=1}^r \alpha_j^2 y_j \right) - \left(\sum_{j=1}^r \alpha_j y_j \right)^2 \right] \\
 &= \left(\sum_{j=1}^r y_j \right)^{-1} \left[\sum_{i=1}^r \left(\sum_{j=1}^r \left(\alpha_j^2 y_i y_j - \alpha_i \alpha_j y_i y_j \right) \right) \right] \\
 &= \left(\sum_{j=1}^r y_j \right)^{-1} \left[\sum_{i=1}^r \left(\sum_{j=1}^i \left(\alpha_j^2 y_i y_j - 2\alpha_i \alpha_j y_i y_j + \alpha_i^2 y_i y_j \right) \right) \right] \\
 &= \left(\sum_{j=1}^r y_j \right)^{-1} \left(\sum_{j < i} y_i y_j (\alpha_j - \alpha_i)^2 \right) \geq 0,
 \end{aligned}$$

which is result i). The proof is completed by noting that $G = 0$ if and only if $\alpha_i = \alpha_j$ for all i and j ; this proves ii).

Now we can prove

Theorem 1: In the chemical equilibrium problem

$$i) \quad \sum_{j=1}^N \frac{\theta_{ij}^2}{y_j} \geq 0$$

$$ii) \quad \sum_{j=1}^N \frac{\theta_{ij}^2}{y_j} = 0 \quad \text{if and only if there exist}$$

numbers $\alpha_1, \alpha_2, \dots, \alpha_p$ such that

$$a) \quad \theta_j = \alpha_{[j]} y_j \quad j \leq n$$

$$b) \quad \theta_j = \alpha_{j-n} S_{j-n} \cdot \quad j > n$$

Proof: The proof follows by noting that for $i > n$

$$\theta_i = \sum_{j \in \langle i-n \rangle} \theta_j \cdot$$

Then,

$$\begin{aligned} \sum_{j=1}^N \frac{\theta_{j \cdot d}^2}{y_j} &= \sum_{j=1}^n \frac{\theta_j^2}{y_j} - \sum_{k=1}^p \frac{\theta_{k+n}^2}{S_k} \\ &= \sum_{k=1}^p \left(\sum_{j \in \langle k \rangle} \frac{\theta_j^2}{y_j} - \frac{\left(\sum_{j \in \langle k \rangle} \theta_j \right)^2}{\sum_{j \in \langle k \rangle} y_j} \right) \geq 0 \end{aligned}$$

by lemma 1. Furthermore, by lemma 1, if the equality holds, then for each k there is a number α_k such that $\theta_j = \alpha_k y_j$ if $j \in k$. This, noting that b) follows from the fact that

$$\theta_i = \sum_{j \in \langle i-n \rangle} \theta_j \quad \text{for } i > n ,$$

completes the proof of the theorem.

Our final result is

Theorem 2: In the chemical equilibrium problem, with (y_1, y_2, \dots, y_n) feasible and $\theta_1, \theta_2, \dots, \theta_n$ calculated as in (4.7)

$$\text{i)} \quad \sum_{j=1}^n \theta_j (c_j + \log \hat{y}_j) \leq 0$$

$$\text{ii)} \quad \sum_{j=1}^n \theta_j (c_j + \log \hat{y}_j) = 0 \quad \text{if and only if}$$

(y_1, y_2, \dots, y_n) is optimal.

Proof: i) follows from Theorem 1, (B.10), and the fact that (y_1, y_2, \dots, y_n) is feasible.

To prove ii), we assume that

$$\sum_{j=1}^n \theta_j (c_j + \log \hat{y}_j) = 0 .$$

Then,

$$\sum_{j=1}^N \frac{\theta_j^2}{y_j} = 0 ,$$

and θ_j is as in ii) of Theorem 1. Combining b) of Theorem 1 and (4.12) we have

$$\theta_{k+n} = S_k \pi'_{m+k} = \alpha_k S_k$$

or

$$\alpha_k = \pi'_{m+k} .$$

Next, we combine a) of Theorem 1 with (4.7) to get

$$\begin{aligned} \theta_j &= y_j \left[\sum_{i=1}^m \pi'_i a_{ij} - c_j - \log \hat{y}_j + \pi'_{[j]+m} \right] \\ &= y_j \alpha_{[j]} = y_j \pi'_{[j]+m} \end{aligned}$$

or

$$\sum_{i=1}^m \pi'_i a_{ij} - c_j - \log \hat{y}_j = 0 .$$

This last result is the optimality condition for (y_1, y_2, \dots, y_n) as given by (1.4), and this demonstrates the forward implication of ii). The converse follows from the fact that optimality implies that the objective function cannot be decreased.

REFERENCES

1. Shapiro, N. Z., and L. S. Shapley, Mass Action Laws and the Gibbs Free Energy Function, The RAND Corporation, RM-3935-1-PR, September 1964.
2. Dantzig, G. B., Linear Programming and Extensions, The RAND Corporation, R-366-PR, August 1963. Also published by Princeton University Press, Princeton, New Jersey, 1963.
3. Kaplan, Wilfred, Advanced Calculus, Addison-Wesley Press, Inc., Cambridge, Massachusetts, 1952.
4. Clasen, R. J., The Linear-Logarithmic Programming Problem, The RAND Corporation, RM-3707-PR, June 1963.
5. White, W. B., S. M. Johnson, and G. B. Dantzig, Chemical Equilibrium in Complex Mixtures, The RAND Corporation, P-1059, October 8, 1957. Also published in J. Chem. Phys., 28 (1958) 751-755.
6. International Business Machines Corporation, "IBM 7040/7044 Operating System, FORTRAN IV Language," IBM Systems Reference Library, Form C28-6329, Poughkeepsie, New York, 1963.
7. Dantzig, G. B., and J. C. DeHaven, "On the Reduction of Certain Multiplicative Chemical Equilibrium Systems to Mathematically Equivalent Additive Systems," J. Chem. Phys., 36 (1962) 2620-2627.
8. Shapiro, N. Z., A Generalized Technique for Eliminating Species in Complex Chemical Equilibrium Calculations, The RAND Corporation, RM-4205-PR, August 1964.
9. Dantzig, G. B., J. C. DeHaven, I. Cooper, S. M. Johnson, E. C. DeLand, H. E. Kanter, and C. F. Sams, "A Mathematical Model of the Human External Respiratory System," Perspectives in Biol. & Med., 4 (1961) 324-376.
10. Maloney, J. V., Jr., M.D., J. C. DeHaven, E. C. DeLand, and G. B. Bradham, M.D., Analysis of Chemical Constituents of Blood by Digital Computer, The RAND Corporation, RM-3541-PR, April 1963.

11. DeHaven, J. C., and E. C. DeLand, Reactions of Hemoglobin and Steady States in the Human Respiratory System: An Investigation Using Mathematical Models and an Electronic Computer, The RAND Corporation, RM-3212-PR, December 1962.
12. DeHaven, J. C., E. C. DeLand, N. S. Assali, and W. Manson, Physiochemical Characteristics of Placental Transfer, The RAND Corporation, P-2565, March 1962.
13. Warga, J., "A Convergent Procedure for Solving the Thermo-Chemical Equilibrium Problem," J. Soc. Indust. Appl. Math., 11 (1963) 594-606.